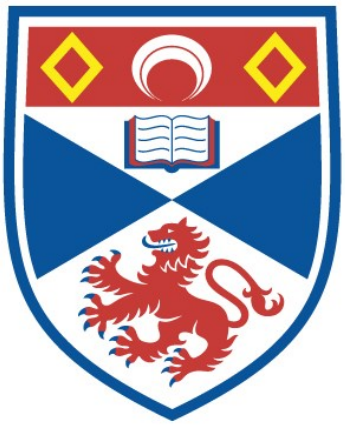
THE THERMAL DECOMPOSITION OF MERCURY DIBENZYL

David Calvert

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1958

THE THERMAL DECOMPOSITION OF MERCURY DIBENZYL.

Being a Thesis presented by David Calvert
to the University of St. Andrews, in application
for the Degree of Doctor of Philosophy.

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Declaration.

I hereby declare that the following Thesis is based on the record of work done by me, that the Thesis is my own composition, and that it has not been presented previously for a Higher Degree.

The researches were carried out in the Chemical Research Laboratories of the United College of the University of St. Andrews, under the supervision of Dr. Charles Horrex.

David Calvert.

12th. May, 1958.

Certificate.

I certify that David Calvert has spent nine terms at Research Work under my supervision, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying Thesis in application for the degree of Doctor of Philosophy.

C. Horrex, Ph.D.,
Director of Research.

University Career.

I first matriculated in the University of St. Andrews in October, 1949. I graduated B.Sc. with First Class Honours in Chemistry in June, 1953.

In August 1953 I was admitted as a Research Student in the University of St. Andrews under Ordinances 16 and 61, and was awarded a Research Scholarship from the Carnegie Trust for the Universities of Scotland, which I held from October, 1953, to September, 1954. In October, 1954, I was appointed as a Temporary Lecturer in Chemistry in the Department of Chemistry of the United College of the University of St. Andrews. I held this appointment until September, 1956. During this latter period, I continued the Researches described in this Thesis on a part time basis.

Acknowledgements.

I wish to record my appreciation to Dr. C. Horrex for supervising the work presented in this Thesis, and for the stimulating interest and encouragement which he has shown throughout the investigations.

I should like to thank the Trustees of the Carnegie Trust for the Universities of Scotland for the Research Scholarship, and Professor John Read, F.R.S., for the laboratory facilities which have been made available.

I am indebted to Mr. A.N. Hamer, B.Sc., for his assistance and helpful discussions on many occasions, and to Mr. T.W. Norris for his guidance and help during the construction of the mass spectrometer.

Mr. C.M. Leslie, Mr. I.R. Sinclair, B.Sc., and Mr. J.D. Pitts kindly prepared the p-nitrobenzyl mercury iodide, the diphenyl picryl hydrazyl and the p-nitrophenyl acetic acid, respectively.

I am grateful to Dr. J.Y. Macdonald and Messers R. Morris and J. Rayne who produced the photographs.

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INTRODUCTION.

There has been a growing interest during the last 25 years in the energies, structures and reactivities of organic radicals in the gaseous phase. Our knowledge of such entities has accumulated mainly through detailed studies of the mechanisms of gaseous pyrolytic reactions. Theoretical calculations have supported many of the experimental conclusions, and, in recent years, new practical techniques such as mass spectrometry, flash photolysis and electron paramagnetic resonance spectroscopy have provided powerful tools for the study of these transient structures.

In spite of our extensive knowledge of the properties of many aliphatic and aromatic radicals (74) it is still not possible to predict with certainty the exact course of reactions in which they take part, and there is a great need for detailed kinetic investigations into their behaviour.

The benzyl radical, in particular, has been credited with considerable stability by several workers (75), while others have suggested that it can attack its own dimer (76). It seemed desirable therefore, to extend our knowledge of the behaviour of this radical by a study of the pyrolysis of some compound which would yield these radicals easily and which would allow only few possibilities for side reactions to occur. Such a projected study would become more valuable if these radicals could be detected directly and their rate of dimerisation determined.

With these aims, mercury dibenzyl was selected as a compound for gaseous phase thermal decomposition studies, and a mass spectrometer was chosen as the analytical apparatus, this instrument being designed so that both stable products and free radicals could be detected and investigated.

It seemed most probable that the mercury-carbon bonds in the compound chosen for the investigation would be relatively weak and, because of the anticipated low temperature for the decomposition, any initial products should not be contaminated with materials from secondary reactions. The pyrolysis of several mercury dialkyls had already been reported and thus some comparative kinetic information was available.

Experience on the construction and operation of a mass spectrometer was available in St. Andrews and thus the possible difficulties in the analytical side of the above project were substantially decreased. The instrument already available was able to analyse only the stable products of pyrolysis experiments, and in order to extend the researches of the Department on the lines indicated, it was decided to construct a new mass spectrometer tube. Eltenton, Lossing and their co-workers had shown how free radicals could be extracted from suitably designed thermal decomposition systems and detected in mass spectrometers (77), (78), and the stability of the benzyl radicals seemed to be a favourable feature for the success of similar experiments with mercury dibenzyl.

Since other work envisaged a new mass spectrometer for the

study of benzyl compounds by electron impact methods, it was possible to collaborate with other research workers on the construction of portions of the new instrument.

Details of the construction of this new mass spectrometer tube and some indications of its performance are given in Part 1 of this thesis.

As the construction of the instrument progressed, work on both the preparation of pure mercury dibenzyl and the determination of its vapour pressure was commenced. It was considered that partial vapour pressures of 0.01-0.001 mm. mercury of reactant would suffice in the kinetic flow system if mass spectrometric analyses were to be used. Unfortunately, the mercury dibenzyl could not be obtained in the vapour phase at even these low partial pressures, because the substance showed a marked tendancy to decompose in the solid phase at temperatures above 100°C. In addition, positive ions of the types $HgBz_2^+$ or $HgBz^+$ could not be obtained in the mass spectrometer from the vapour of this compound under electron bombardment, thus rendering analyses for the compound using such techniques more difficult than they might have been.

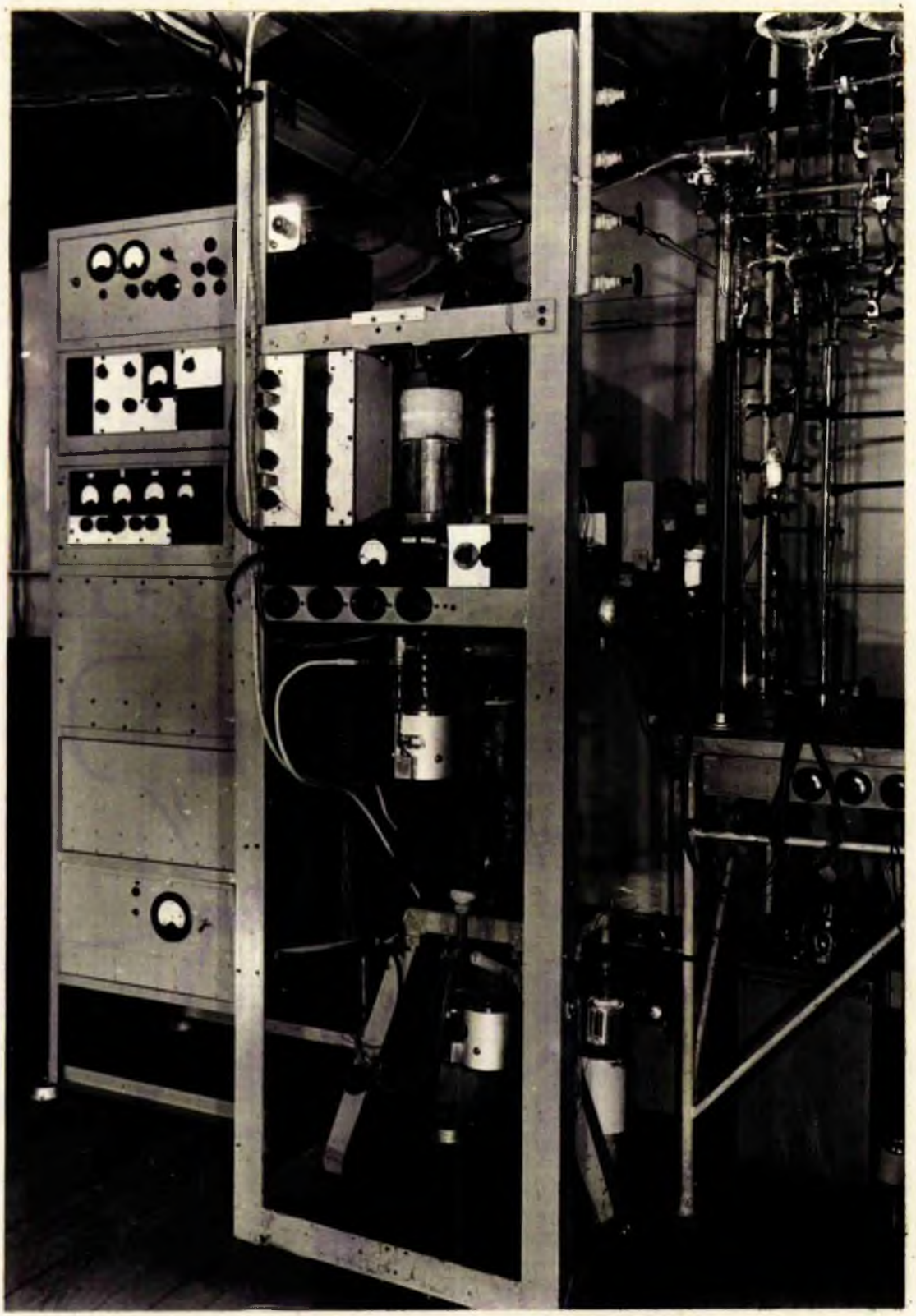
It was therefore decided to study the decomposition of this material in solution in an inert solvent. Part 2 of this thesis is an outline of the methods used and the results obtained during the investigation of the decomposition and its mechanism, during which the older mass spectrometer was used to identify some of the solid products formed.

PART 1.

THE CONSTRUCTION OF A MASS SPECTROMETER.

FIGURE 1.

Fig. 1.



A front view of the mass spectrometer, together with parts of the electronic controls and the gas handling system.

THE GENERAL PRINCIPLES OF A MASS SPECTROMETER.

The physical principles on which the operation of a mass spectrometer depend are as follows :-

The trajectory of an ion, of mass m gm. and charge e e.s.u., travelling with uniform velocity v cm./sec. perpendicularly into the plane edge of a sharply defined uniform magnetic field of strength H e.s.u. will be an arc of radius r cm. such that

$$r = mv/He \quad , \qquad \ldots\ldots (1)$$

assuming that the ion velocity is much less than the velocity of light, so that no relativistic corrections are necessary. Thus, each of several ions of different momenta and charge travelling a common path into the magnetic field will, in general, describe arcs of different radii within the field.

If, however, all the ions (assumed to be initially at rest) are given large kinetic energies by initial passage through a high potential of V e.s.u., we have

$$\tfrac{1}{2}mv^2 = eV \quad , \qquad \ldots\ldots (2)$$

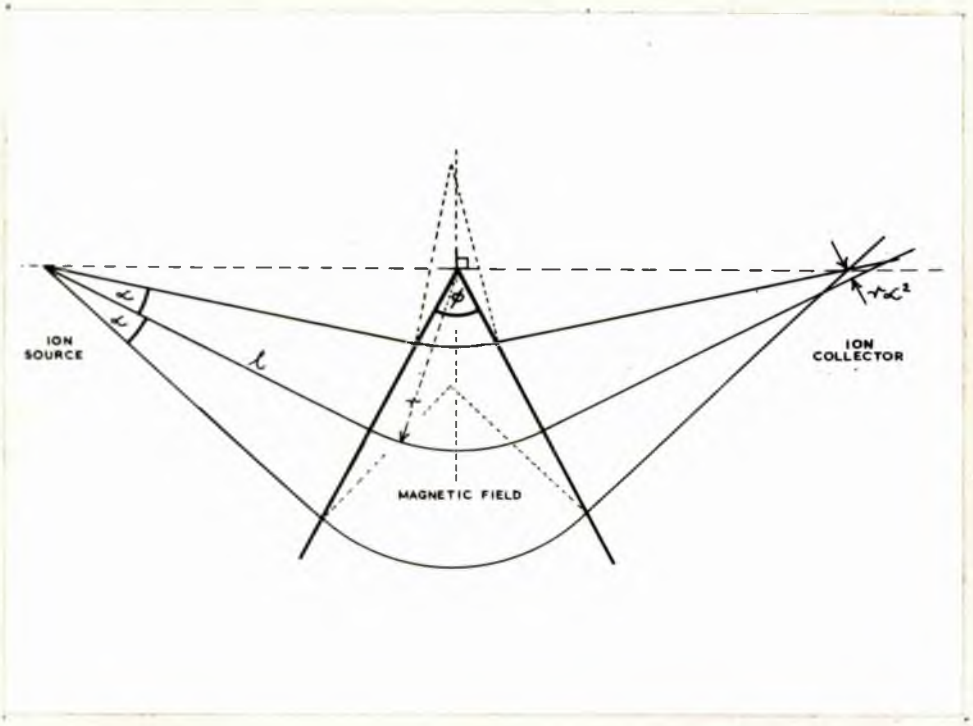
and now the magnetic system will perform mass separations because all ions of the same mass to charge ratio will, in the magnetic field, traverse the same arc whose radius of curvature will be proportional to $\sqrt{\text{mass}}$, thus :

$$r = \frac{1}{H}\sqrt{\frac{2mV}{e}} \quad . \qquad \ldots\ldots (3)$$

The earliest mass spectrometers had magnetic fields which

FIGURE 2.

Fig. 2.



The path of a homogeneous ion beam through a sector magnetic field.

deflected the ions through angles of 180°, but mathematical analyses by Barber, Stephens and Hughes (1), (2), (3), indicated that sector magnetic fields of smaller angles could be used, thus allowing a considerable reduction of magnet size.

The path of a slightly diverging homogeneous ion beam through a sector field is indicated in Fig. 2. The general conditions for the first-order refocussing of ion beams deflected by magnetic fields have been discussed by Herzog, and the application of his general equations to the symmetrical mass analyser indicated in Fig. 2 leads to the condition that

$$l = r(\cot \phi + \operatorname{cosec} \phi).$$

Modern instruments usually have ϕ equal to 60° or 90°, and r is usually chosen to be 6". The choice of these particular parameters for any given instrument is usually a matter for some compromise.

The mass dispersion, D, between mono-energetic ions of masses M and $M+\delta M$ produced at the plane of the collector slit in a symmetrical instrument is given by

$$D = r.\, \delta M/M .$$

As the size of the sector angle ϕ decreases, the size of the magnet required is reduced, but, for a given value of r, the ion path between the source and collector is lengthened. Thus, at small values of ϕ, higher vacua are required to increase the mean free path of the ions and thus prevent loss of ions from

the beam by collision.

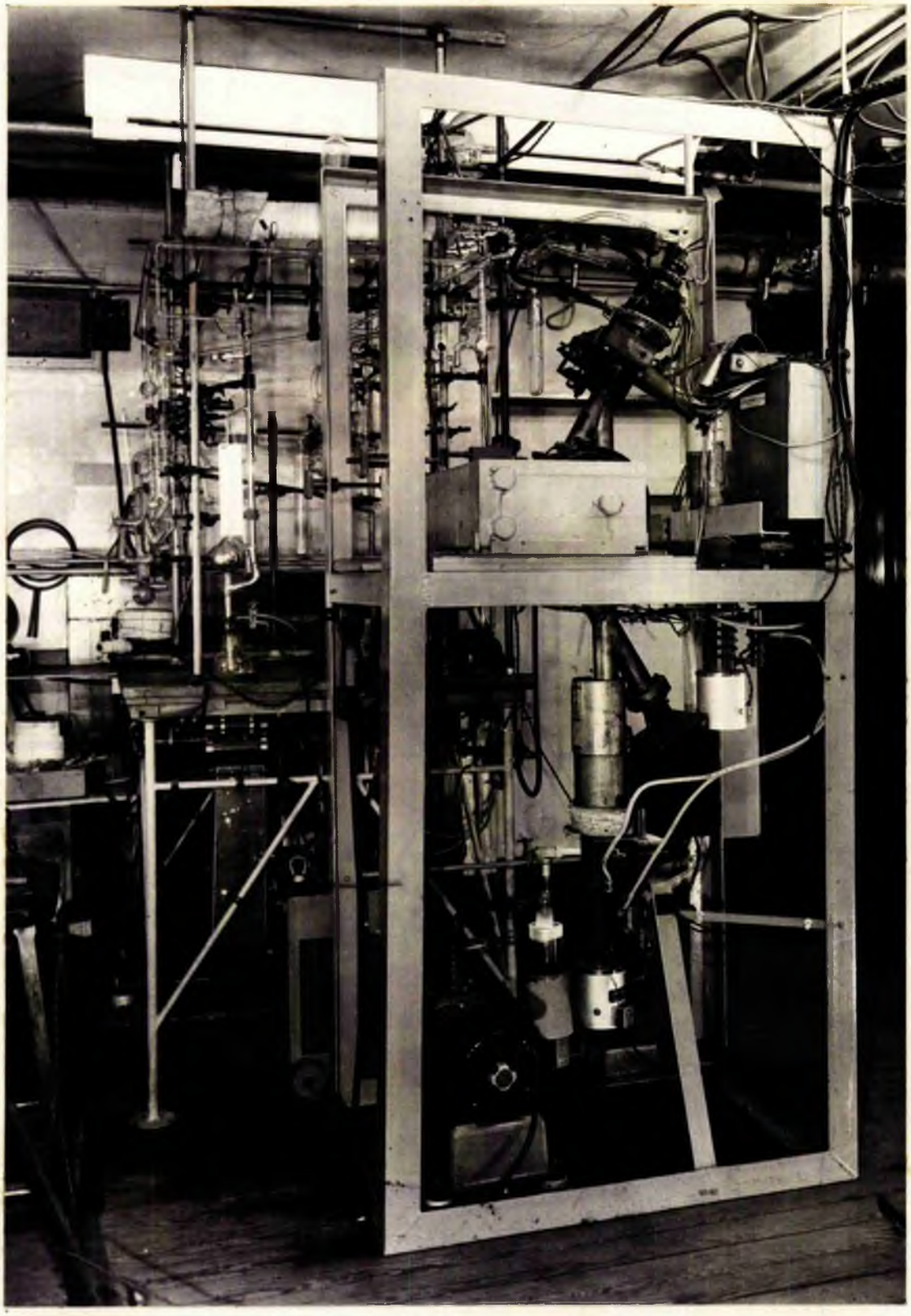
The instrument described below was built with r = 6" and $\phi = 60^{\circ}$, thus combining reasonable resolution with an economical size of magnet.

As is indicated in Fig. 2, in practical instances perfect refocussing of the ion beam is not possible, because the divergence of the ion beam leaving the source results in a spherical aberration of $2r(1-\cos\alpha)$, where α is the half-angle of spread. When α is small, this aberration is approximately $r.\alpha^2$. Other aberrations which affect the cross section of the ion beam have been discussed by Barnard (4).

To allow the ions to follow their correct tracks, their mean free paths must be greater than the source to collector distance. The source, collector and the intermediate regions have therefore to be enclosed in a gas-tight envelope which is evacuated to low pressures, usually less than 10^{-6}mm.

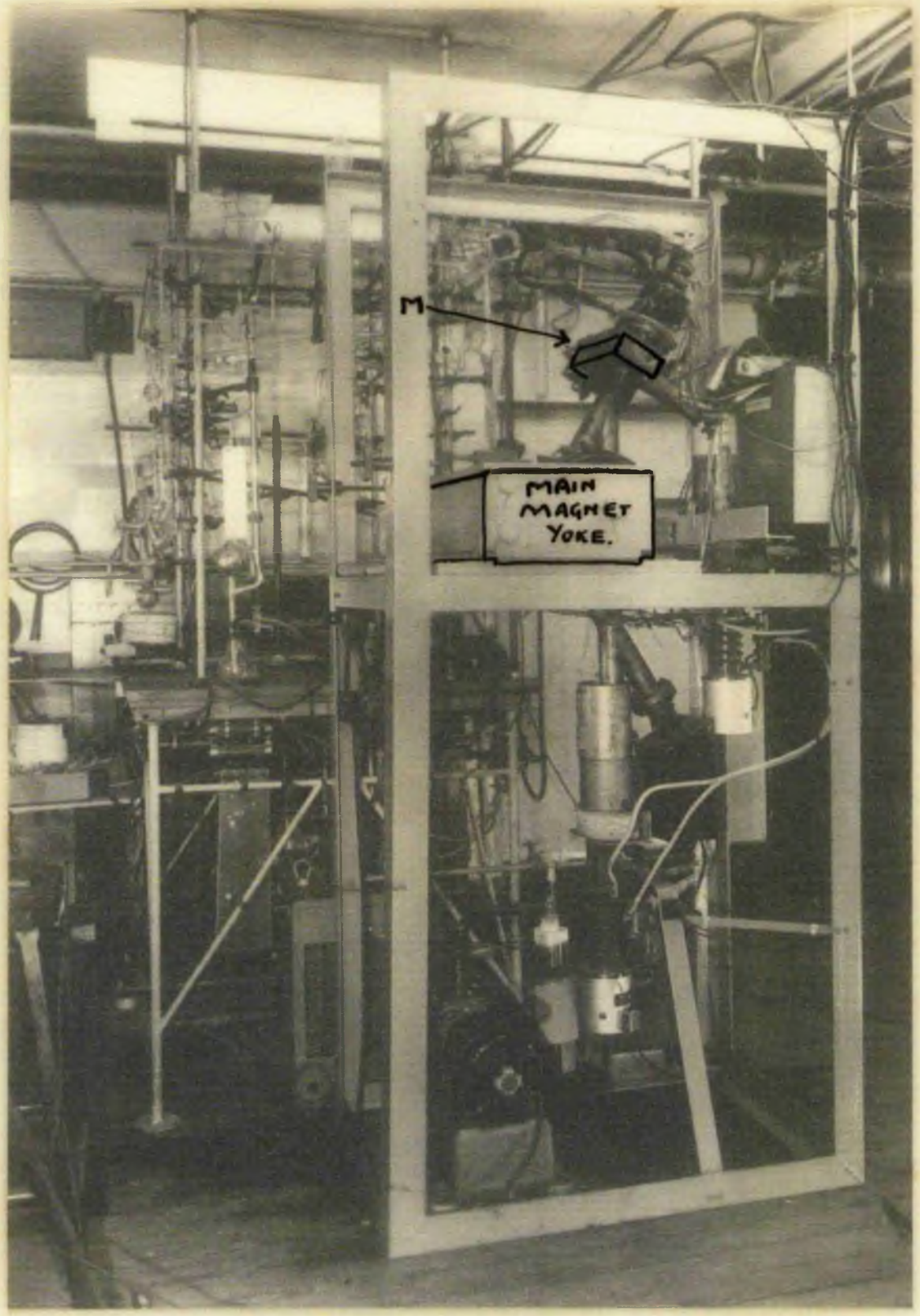
FIGURE 3.

Fig. 3.



A side view of the mass spectrometer.

Fig. 3.



A side view of the mass spectrometer.

FIGURE 3.

THE NEW MASS SPECTROMETER.

The General Design.

Our interest in benzyl compounds required that the new mass spectrometer should have a resolving power of at least 1 in 150 atomic mass units, sufficient to detect benzyl ions (91 a.m.u.) with certainty, whilst our desire to study in detail the results of pyrolysis experiments required that a small moveable furnace should be placed near a fine leak which was to be positioned directly over the ionisation chamber of the instrument.

The electrical controls of the instrument should enable accurate control and measurement to be made of the energies of the ionising electrons. Thus, during a pyrolysis reaction in the furnace, any radicals produced which were sucked through the leak into the ionisation chamber could be ionised and detected in preference to similar ions formed at higher electron energies from molecular species.

As it was planned to study the pyrolyses of organic compounds of mercury, in particular mercury dibenzyl, oil diffusion pumps were selected in preference to mercury diffusion pumps. In addition, the required instrument had to be adaptable for routine gas analyses.

The original mass spectrometer in the Chemistry Department at St. Andrews was not suited to this type of investigation, having been provided with a mercury diffusion pump for the analysis of gases of low molecular weight, and a second instrument

FIGURE 4.

Fig. 4.

The mass spectrometer tube unit.

was therefore designed by Mr. A.N. Hamer, B.Sc., and built by the author in collaboration with Mr. Hamer and Mr. R.C. Naylor, B.Sc.

The general features of the completed instrument can be seen in Figs. 1 and 3.

The Mass Spectrometer Tube Unit.

The tube unit, shown in Fig. 4, forms most of the gas-tight envelope for the instrument and also correctly locates the ion source and ion collector units.

The main components of the tube were machined from inconel tubes, the flanges were machined from inconel plate and the bend was formed from a copper tube. The nickel-chromium-iron alloy inconel (Messrs Henry Wiggin & Co.) was selected because of its relative freedom from absorbed gases and for its non-magnetic properties.

Previous experience suggested that the ion source and ion collector units should be easily accessible for cleaning and adjusting; each was therefore mounted on pillars supported from a large flange which could be bolted to a corresponding flange on the tube unit. A vacuum seal between each pair of flanges was obtained by the use of a Fluon or Gaco ring gasket T, Fig. 5, which lay in a machined recess in one flange and which was trapped by a corresponding projection on the other flange.

To attain adequate mechanical strength in the tube and

TABLE 1.

Table 1.

Some errors present in the completed tube unit.

The acute angle between the two main flanges, ϕ in Fig. 4, measured in the plane of the tube unit, should have been 60°. By certain measurements and calculations this angle was found to be 60° 32'.

Two points, X and Y in Fig. 4, which represented the positions of the exit slit of the ion source unit and the entry slit of the ion collector unit, were marked on two of the pre-assembled parts of the tube unit. These points should have been 24" apart in the assembled unit. By measurement, they were found to be 23.98" apart in the completed tube.

to assist the pumping efficiency, a vertical cross connection was provided from the source to the collector region.

All the individual components for the tube unit were machined or milled to the closest tolerances, and were checked before assembly. All the joints were made with either high or low m.pt. Easy-Flo silver solder.

The relative orientation of the two large flanges on the tube unit is the most critical factor in the whole of the assembly, and joint J, Fig. 4, was made with the two pre-assembled parts of the tube mounted on specially constructed jigs which were bolted in the correct relative positions on the table of a milling machine. The most careful checks were made both before and after this joint was soldered to ensure the correct alignment of the two flanges. The mechanical errors present in the tube unit when completed are indicated in Table 1. The cold traps were added to the tube unit after these alignment tests had been performed.

Each joint in the whole instrument had eventually to be gas-tight. The initial vacuum testing was performed by pumping the tube on a conventional high vacuum system and locating large leaks with either carbon tetrachloride as probe, and a tesla coil discharge in a glass section of the pumping line as detector, or with a hydrogen probe and a Pirani gauge detector. Smaller leaks could be located by measuring the rate of leak into the evacuated tube with a

McLeod gauge, then covering each joint or part of a joint in turn with collodion dissolved in ether and remeasuring the rate of leak.

The smallest leaks could be detected by coupling the tube unit directly to the mass spectrometer already available and using hydrogen or carbon dioxide as a probe gas. Ultimately, the tube and completed instrument was leak tested as its own mass spectrometer using hydrogen, carbon dioxide or carbon tetrachloride as probe material.

The differential pumping design, which is discussed below, required two diffusion pumps, each with a cold trap. These cold traps were made an integral part of the tube unit, and bolted to them were two angle iron plates, milled areas of which provided three places of support for the whole unit.

The tube was mounted within the main frame on three 1" diameter steel balls which were adjustable in a vertical direction. This mounting was such as to allow small rotational and translational movements both about and along three mutually perpendicular axes, and permitted the tube to be placed correctly with respect to the magnet. Initial placing was performed by measurement, without making any allowance for possible fringing effects of the main magnetic field, and subsequent fine adjustments were made with the completed instrument until optimum resolution had been obtained.

The Ion Source and Ion Collector Units.

It is known that decomposition of materials injected for

FIGURE 5.

Fig. 5.

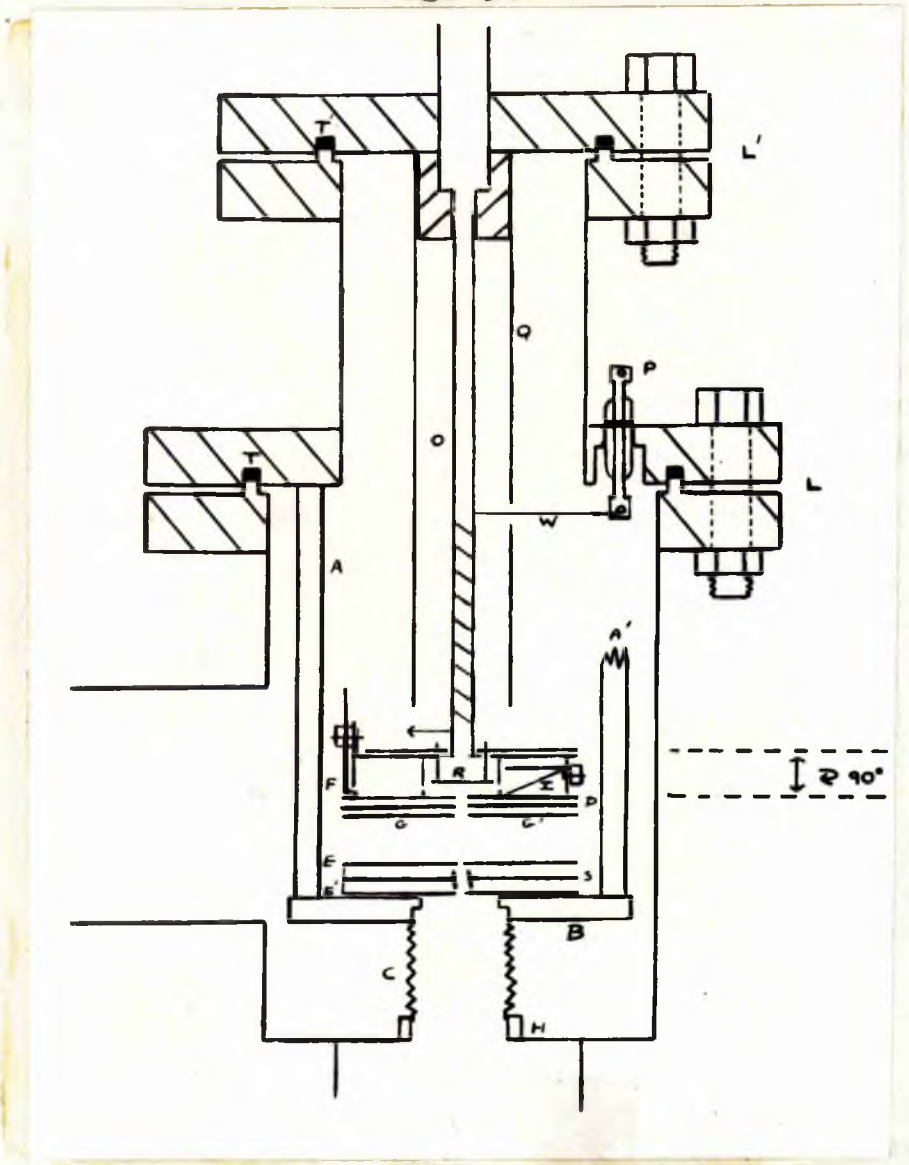


Diagram of the ion source unit.

(The part of the diagram between the dotted lines is a side elevation.)

analysis can occur within a mass spectrometer in the region of the hot filament (5). Subsequent diffusion of these pyrolysis products to the ionisation chamber can then lead to ions which contaminate the mass spectra of the parent materials. To reduce this back diffusion to a minimum a special source design was developed, as indicated in Fig. 5, which allowed differential pumping to be applied across the filament region.

The use of circular glass spacer rings to separate the various electrodes D, G, G', E, E', S, in the ion source unit and the provision of a bellows C below the plate B allowed materials which entered the ionisation chamber via the inlet tube O to be pumped out by two separate routes; either through the slits in the various electrodes or through the slits in the two plates which collimated the electron beam from the filament. Thus, any materials which were pyrolysed on the filament were pumped away from the ionisation chamber. A comparison of the results obtained from the completed instrument with and without the operation of such differential pumping indicated a reduction in contamination of mass spectra from pyrolysis products whenever differential pumping was employed (6).

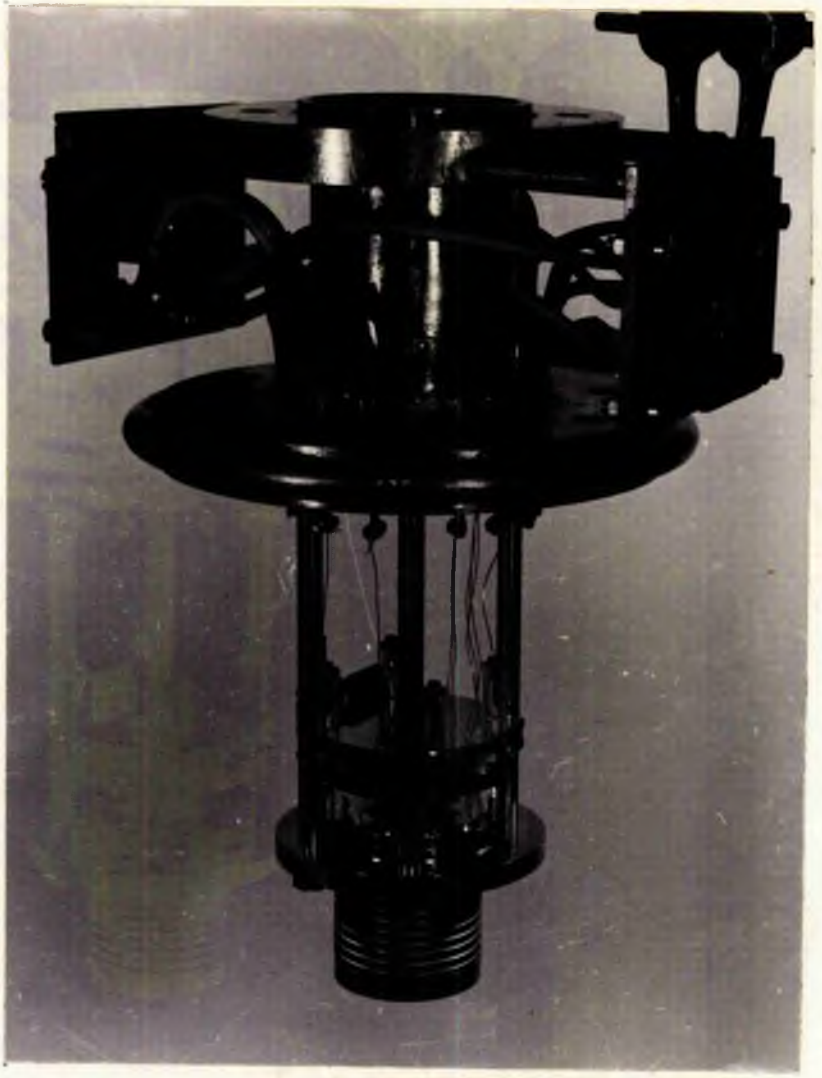
The general features of the ion source and ion collector units can be seen in Figs. 6, 7, 8, 9.

These units, constructed from inconel, nichrome V and stainless non-magnetic steel, were mounted from plates carried on inconel pillars fixed to the main flanges.

The ionisation box, Fig. 8, machined from nichrome V,

FIGURE 6.

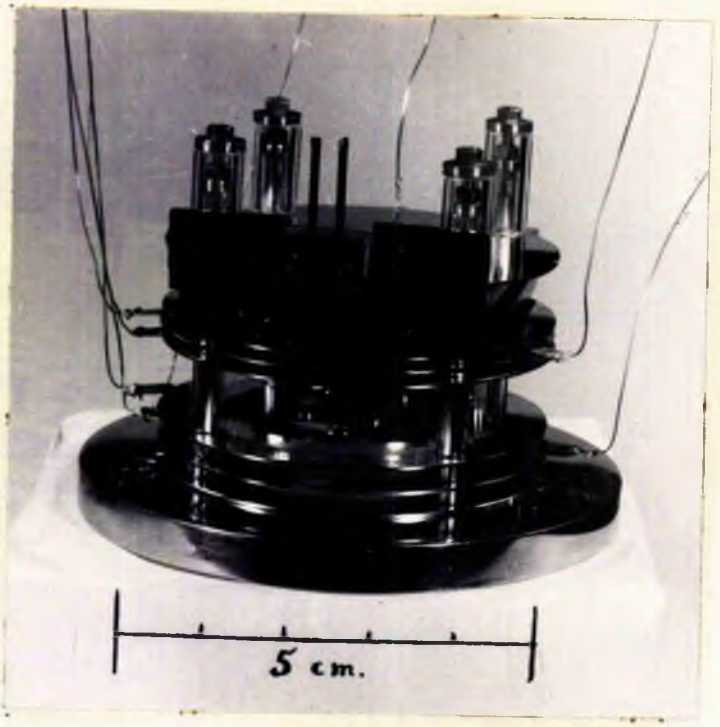
Fig. 6.



The assembled ion source unit mounted from the upper main flange.

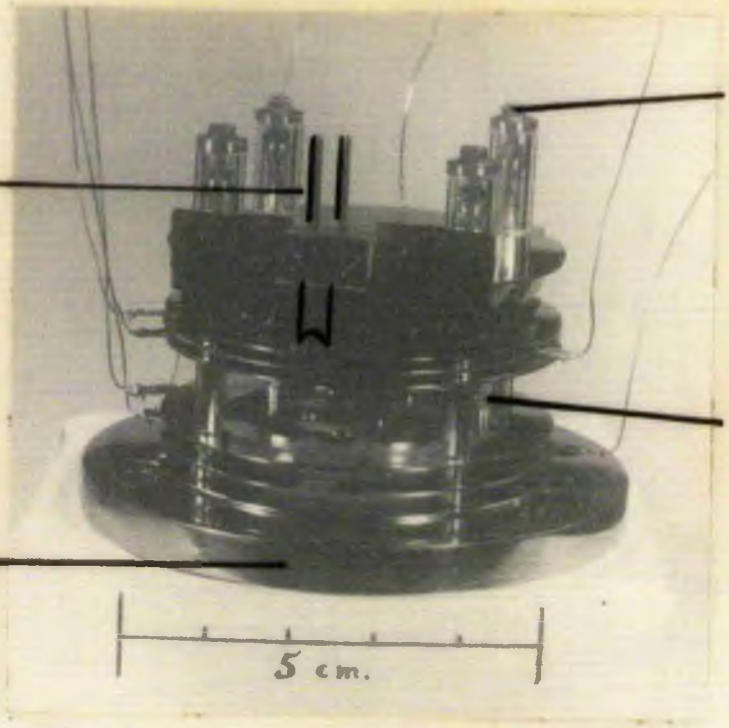
FIGURE 7.

Fig. 7.



The ion source unit. (Full size).

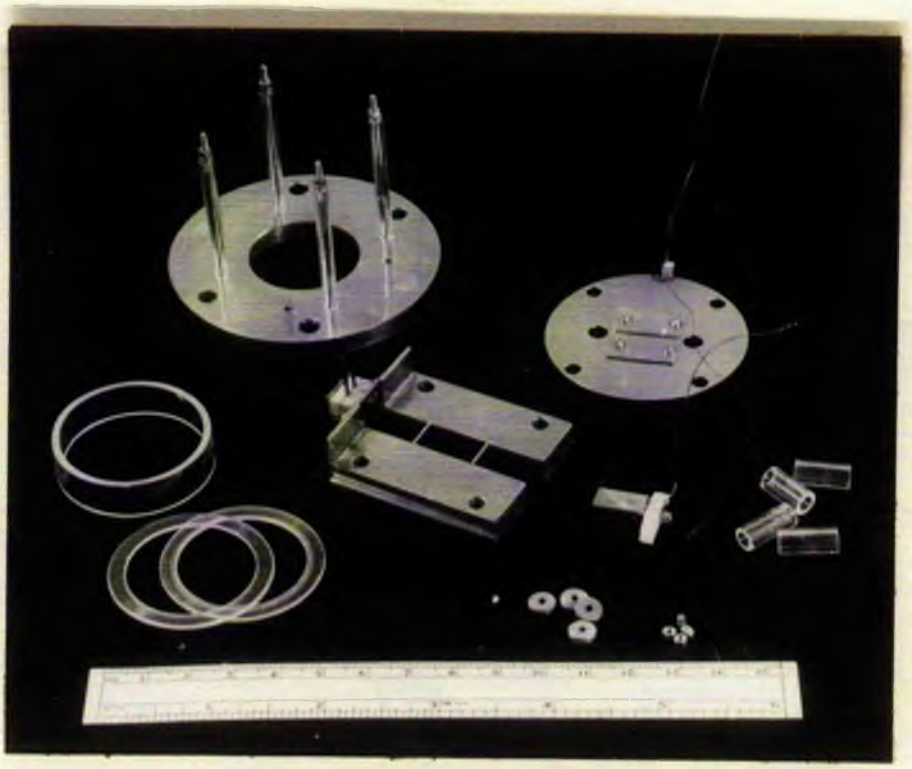
Fig. 7.



The ion source unit. (Full size).

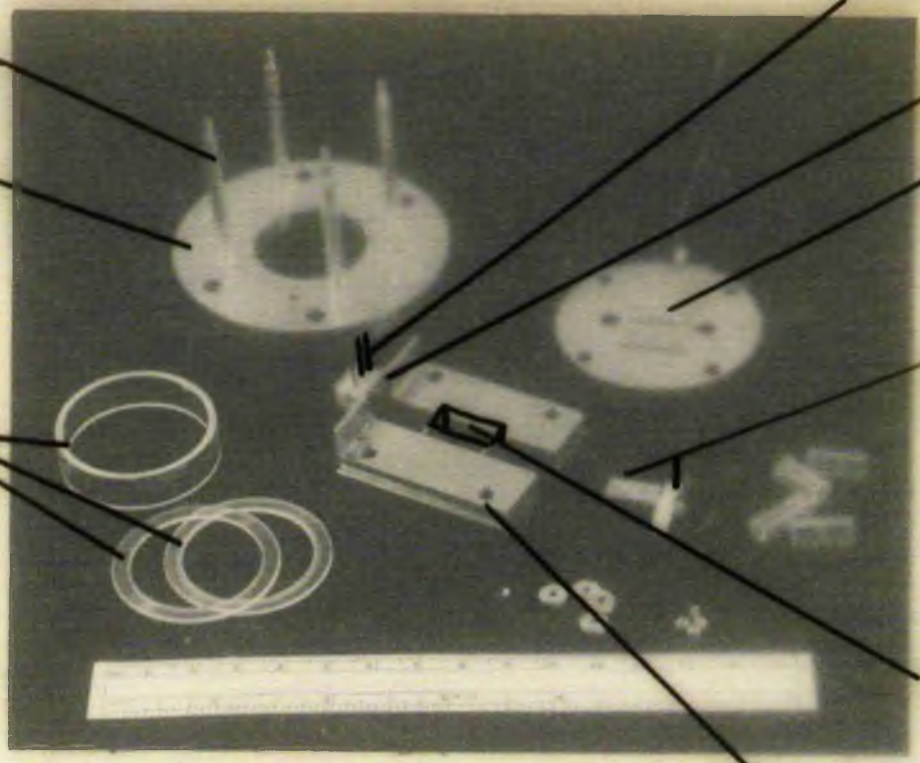
FIGURE 7.

Fig. 8.



Some of the components of the ion source unit.

FIGURE 8.



Some of the components of the ion source unit.

FIGURE 8.

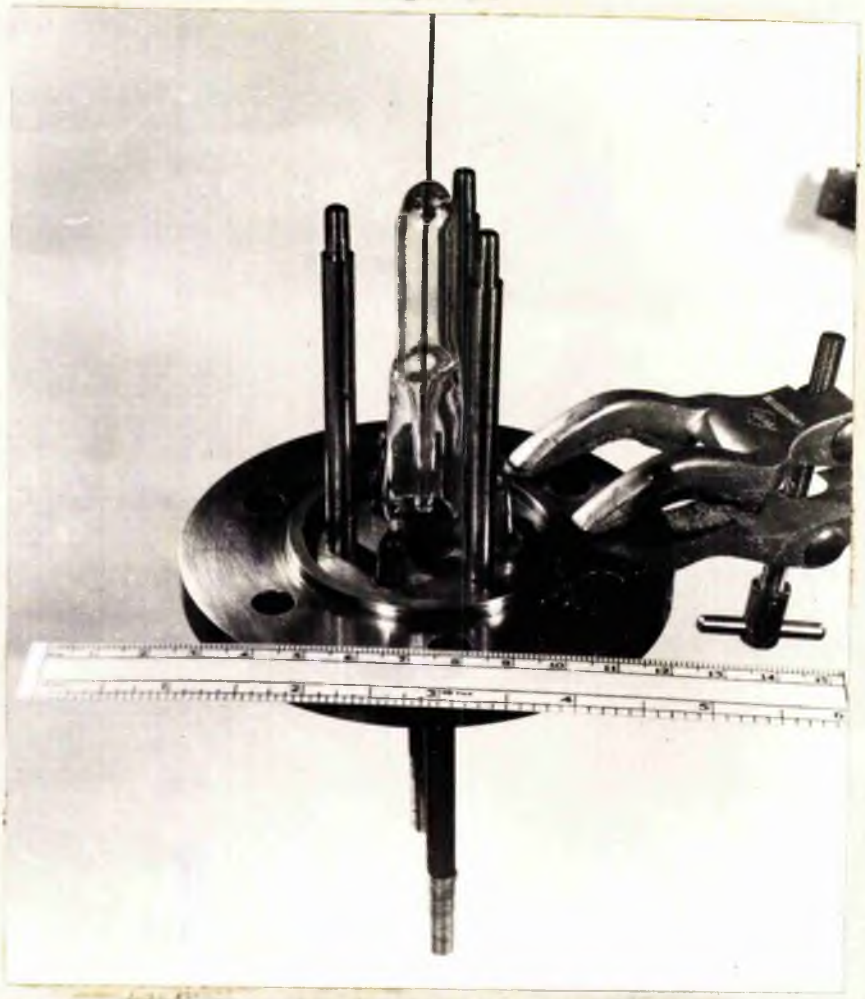
carried at one end a filament (F, Fig. 5) of tungsten ribbon (0.4" approx. x 0.03" x 0.001") spot-welded to two 20 S.W.G. nilo-K wires supported from baked steatite insulator blocks. The electrons emitted from the filament fell through a potential to the first slit, then passed a second slit and entered the ionisation chamber. The electrons crossing the chamber and passing a third slit were collected on an insulated electrode I, Fig. 5. This electron beam was collimated by the field from an externally mounted magnet (M, Fig. 3). The long electron path enabled a simple reactor (O and W, Fig. 5) to be placed directly above the ionisation box. This was used to produce benzyl radicals from dibenzyl (6).

The positive ions formed in suitable regions of the ionisation chamber were expelled through a slit in the lower side of the chamber by a repeller electrode (R, Fig. 5) maintained at a potential about 12 volts above that of the chamber (which was itself usually 2000 volts positive with respect to earth); they then passed through slits in a series of stainless steel electrodes at various potentials which imparted high energies to the ions and which acted as a defining system to collimate the ion beam before it entered the main magnetic field. The slits in two of these electrodes could be pre-adjusted (usually to 0.008" wide) to provide ion beams of various widths.

The potentials applied to the various plates of the ion gun were similar to those recommended by Nier (7), and were selected experimentally to give the highest sensitivity and best resolution.

FIGURE 9.

Fig. 9.



The lower main flange, showing the three mounting pillars for the ion collector unit, and the electrical lead which supported the ion collector electrode.

The collector unit consisted of a defining slit of variable width (usually 0.030" wide) in a plate held at earth potential, followed by a secondary emission suppressor electrode, usually held at -80 volts, beneath which was the collector. The collector, in order to obtain high insulation, was carried on a nilo-K wire sealed into the upper end of a C 40 glass tube whose lower end formed the glass to metal seal in the main flange (see Fig. 9).

The basic constructions of both the source and collector units were similar. The base plate of the source (B, Fig. 5) carried four stainless steel pillars over which fitted glass tubing insulators (Fig. 8). These glass tubes formed the guides for the electrodes, which were insulated from each other by glass spacer rings cut from glass sheet of the correct thickness. The ionisation chamber was also drilled to fit on these glass tubes. The slits in the stack of plates were then correctly aligned by an optical testing procedure, and the whole stack was then clamped together by 10 B.A. stainless steel locking nuts at the top of the steel pillars (Fig. 7).

The electrical leads required for these two units were (with the exception of the collector lead mentioned above) brought through the main flanges by commercial metal to glass high voltage vacuum seals (P, Fig. 5; Edison-Swan, Type 252). These were originally soft-soldered directly into the main flanges on areas which had been covered with Easy-Flo silver solder and then machined, but this proved unsatisfactory as many leaks developed between the metal of the seals and the

main flanges. "Araldite", type 1, (Messrs Aero Research Ltd.) was applied over the commercial seals and was for a time somewhat more satisfactory, but this material eventually pealed from the main flanges and leaks again resulted. Finally the seals were soft-soldered into the flared ends of small lengths of cupro-nickel tubes which had been silver soldered into the main flanges. This method proved entirely satisfactory, and it enabled individual seals to be easily replaced, if necessary.

A moisture and light proof box was rigidly attached to the outside of the main flange of the collector unit. This box housed the electrometer valve V 1 (Fig. 13), the associated high resistors R 1 and R 2, the condenser C 1 and the highly insulated switch S 1 mounted on glass rods. This switch could be operated from outside the box.

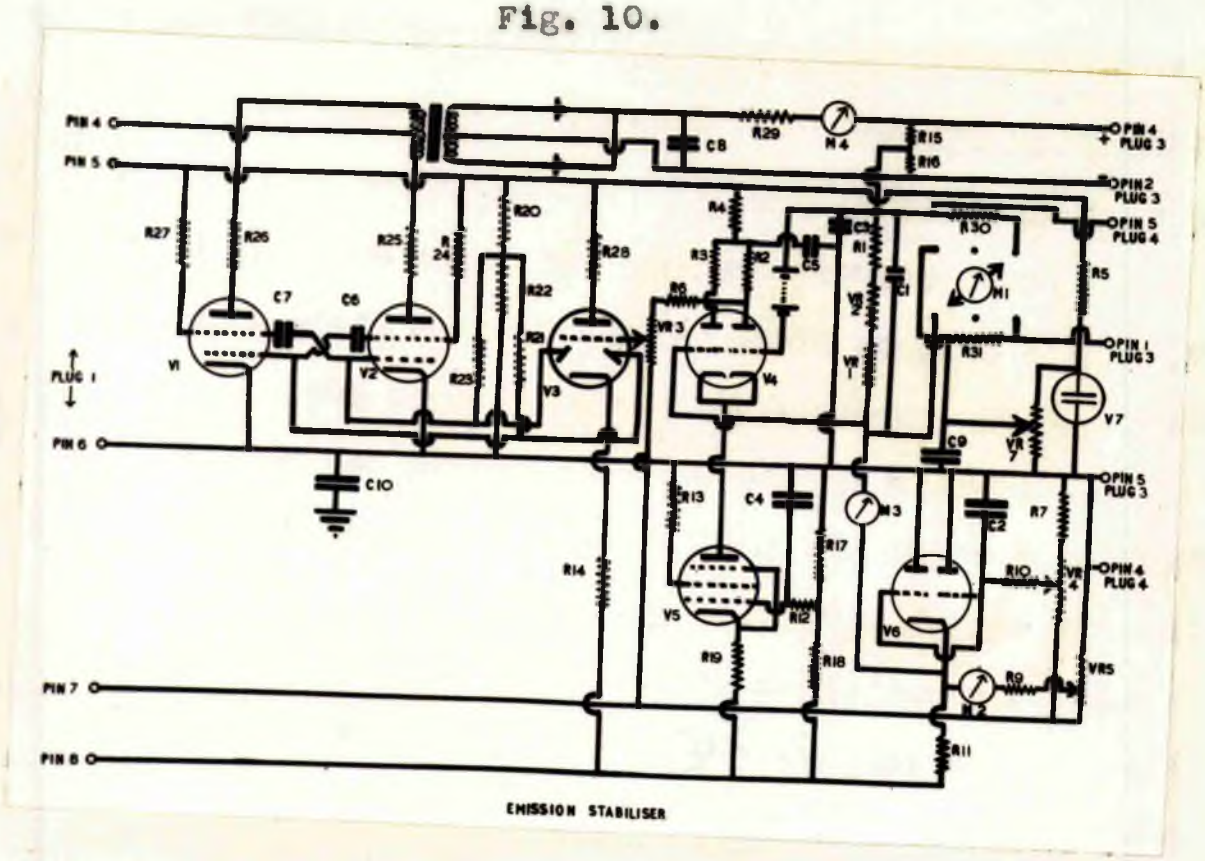
The Magnet.

The magnet yoke, seen in Figs. 1 and 3, was constructed from slabs of Low Moor iron, bolted together at milled bearing faces. The end planes of the 4" diameter cylindrical cores and the four faces of the sector pole caps were made parallel to $\pm$ 0.001" by turning and surface grinding respectively, and the inner faces of the assembled yoke were milled parallel to a similar tolerance. The components, together with two pre-wound coils of total resistance 3,400 ohms, were bolted rigidly together.

The lower faces of the side arms of the yoke were milled

FIGURE 10.

Fig. 10.



The filament emission current stabiliser.

R	1	15	k	R	23	470	k	V	1	12E1	
	2	47	k		24	10	k		2	12E1	
	3	47	k		25	33	ohms		3	DH63	
	4	27	k		26	33	ohms		4	ECC35	
	5	25	k		27	10	k		5	EF37	
	6	470	k		28	1.2	k		6	ECC91	
	7	8	k		29	0.4	ohm		7	85A1	
	9	2	M		30	2	M				
	10	470	k		31	8.2	k	C	1	0.01	µF
	11	50	k						2	0.1	µF
	12	470	k	VR	1	1	M		3	1.0	µF
	13	1	k		2	50	k		4	0.1	µF
	14	100	k		3	1	M		5	4.0	µF
	15	18	ohms		4	25	k helipot		6	470	pF
	16	18	ohms		5	200	k		7	470	pF
	17	330	k		7	50	k		8	150	µF
	18	33	k						9	1	µF
	19	10	k	M	1	50	µamp.		10	1	µF
	20	47	k		2	50	µamp.				
	21	470	k		3	1	mamp.				
	22	47	k		4	5	amp.	B	1	48	volts.

Plug 1 Input from Emission Stabiliser Power Pack.
Plug 3 Output to ion source unit. Plug 4 To Valve Voltmeter.

to carry guides for roller bearings which moved in ways bolted to the horizontal members of the main frame of the instrument. This mounting allowed fine horizontal movement of the 300 lb. magnet, controlled by screwed rods supported in the main frame.

The direct current through the coils could be varied from 4 ma. to 135 ma., at which latter value a field of approximately 5,000 gauss was produced in the 9/16" pole gap.

A small brass spacer was inserted in the pole gap to prevent distortion of the yoke at high field strengths by the mutual attraction between the poles.

The non-parallelism error across the vertical axis of the pole gap of the completed magnet was ±0.0015" , and ±0.002" across the horizontal axis.

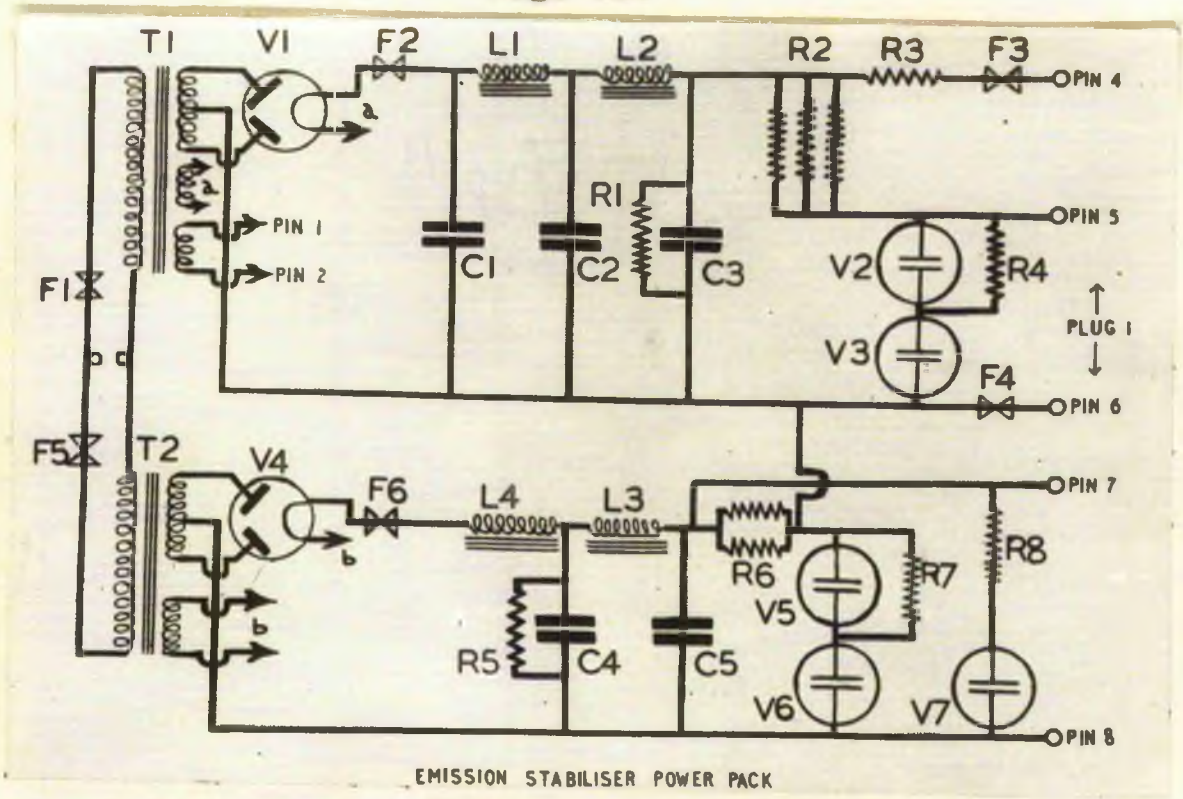
The Electrical Circuits.

The author was not directly concerned with the construction or testing of these items, but a brief description is given for the sake of completeness. Full details are given by Hamer (6) and Naylor (8).

The Filament Emission Current Stabiliser.

In this unit, Fig. 10, which has been described elsewhere (9), a multivibrator circuit (V 1, V 2) supplied a square wave output which was rectified, smoothed and fed to the filament (pins 2 and 4, plug 3). The emission current from the filament to the ionisation chamber (pin 5, plug 3) caused a potential drop along VR 1 + VR 2 + R 1 which was backed off by a reference battery and applied to the signal grid of V 4, whose coupled

Fig. 11.



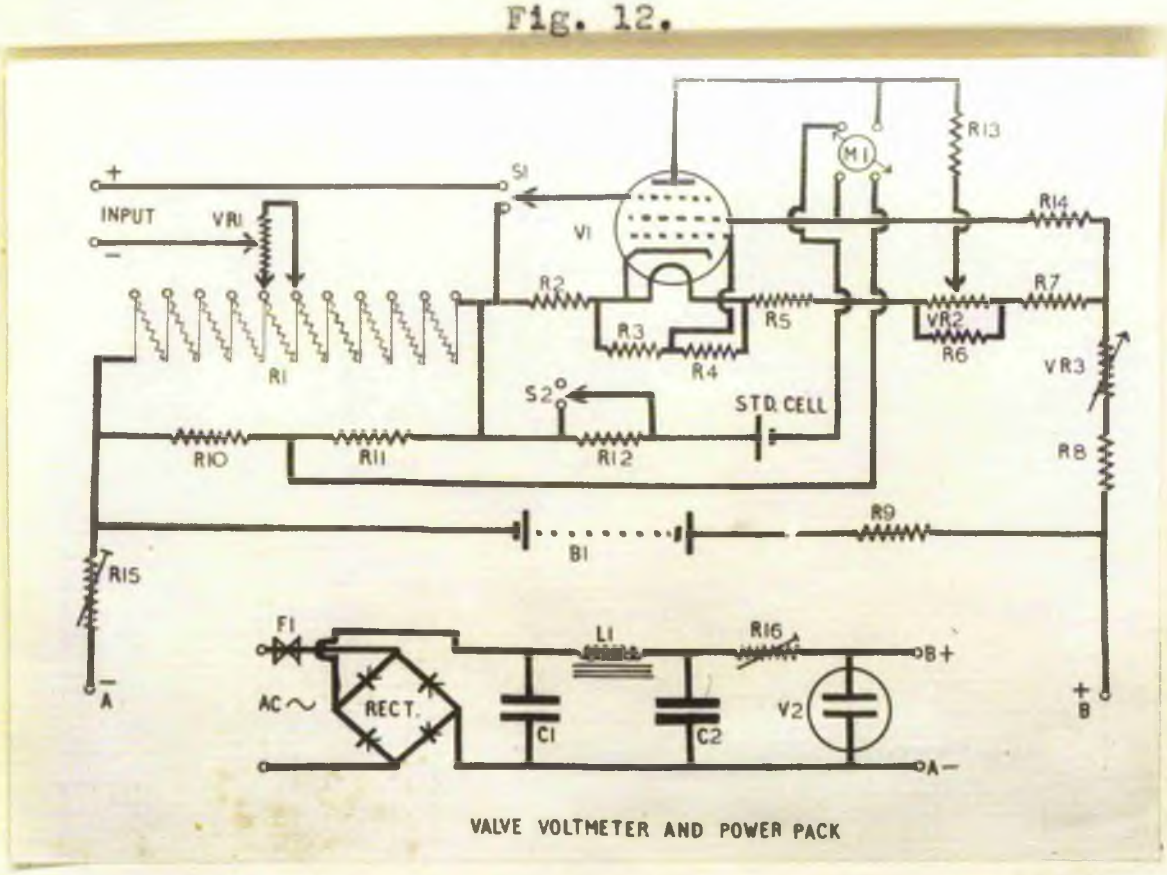
EMISSION STABILISER POWER PACK

R 1	470 k	
2	25k//25k//5k	
3	680 ohms	
4	1 M	
5	470 k	
6	20k//4k	
7	1 M	
8	25 k	
V 1	FW4-500	
2	VR105	
3	VR150	
4	5Z4G	
5	VR150	
6	VR150	
7	VR150	
L 1	5 H	
2	50 H	
3	10 H	
4	5 H	
C 1	6 µF	
2	24 µF	
3	30 µF	
4	6 µF	
5	6 µF	
F 1	3 amp.	
2	1 amp.	
3	250 mamp.	
4	500 mamp.	
5	1.5 amp.	
6	250 mamp.	
T 1	500-0-500 v.,	250 mamp.
	6.3 v.,	5amp.
	4.0 v.,	4amp.
T 2	400-0-400 v.,	100 mamp.
	5 v.,	3amp.

Plug 1 Output to the filament emission current stabiliser.

FIGURE 11.

Fig. 12.



VALVE VOLTMETER AND POWER PACK

R	1	10 x (100 0.1) ohms	VR	1	100 k helipot.
	2	25 ohms		2	100 ohms
	3	22 k		3	100 ohms
	4	10 k			
	5	110 ohms	V	1	954
	6	5 ohms		2	VR105
	7	15 ohms			
	8	18 ohms	M	1	30-0-30 μamp.
	9	3 x 240 ohms in //			
	10	237.3 0.2 ohms	L	1	10 H
	11	12.73 0.01 ohms			
	12	2.7 k	B	1	50 volt accumulator.
	13	20 k variable			
	14	20k//100k	F	1	1 amp.
	15	2 x 300 ohms			
	16	3 x 300 ohms	C	1	24 μF
				2	24 μF

FIGURE 12.

cathodes drew constant current from the anode of V 5.

Any change in the potential drop down VR 1 + VR 2 + R 1 was detected by V 4, was amplified and fed back with the correct sign to the multivibrator circuit, via the cathode follower V 3.

The electron energy, i.e. the potential difference between the filament and the ionisation chamber, was varied by VR 4 which was connected to the grids of the cathode follower V 6, whose cathode controlled the potential of the negative end of VR 1.

The emission current could be varied from 0.1 to 1.0 ma., the electron energy could be varied from 5 to 95 volts, and the trap (i.e. the insulated electrode I, Fig. 5) to ionisation chamber voltage could be varied from 0 to 80 volts.

The A.C. ripple present on the filament current was approximately 0.1%.

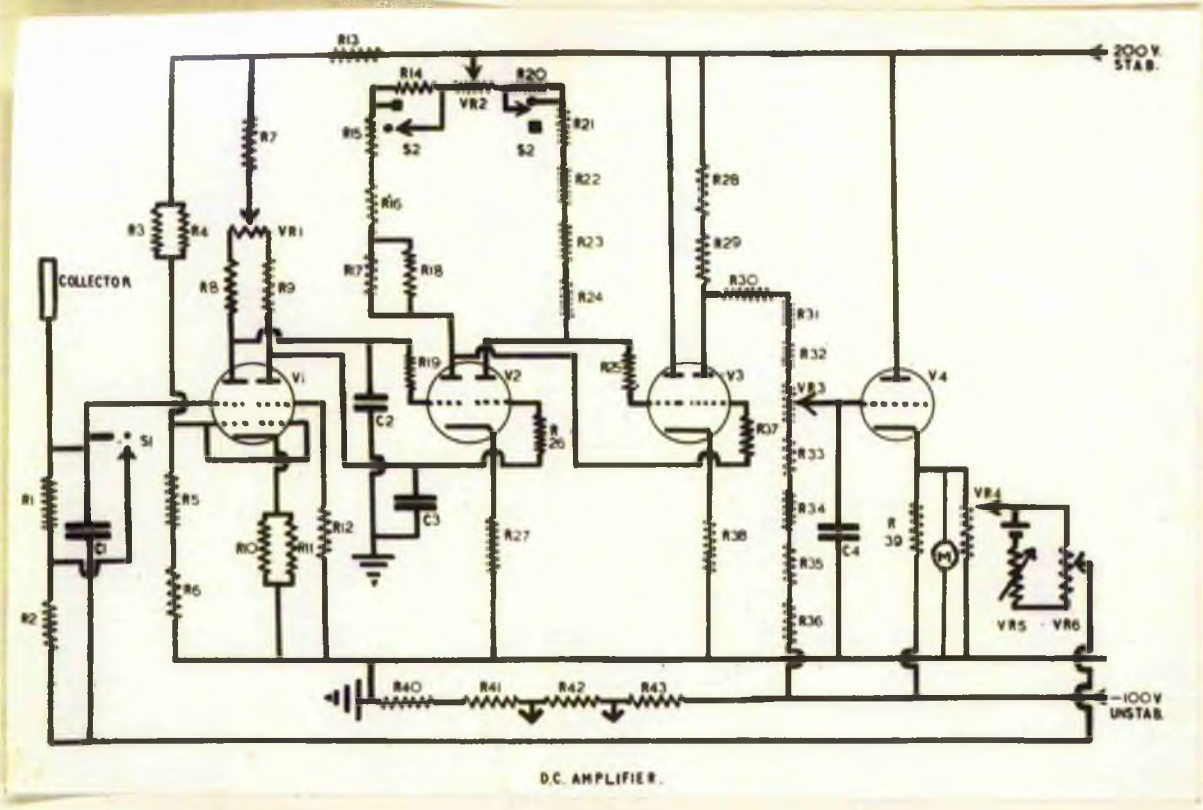
The stabilised voltages required at plug 1 were provided from a conventional power supply, shown in Fig. 11.

The Valve Voltmeter.

The electron energies were measured by a valve voltmeter (Fig. 12) using a 954 acorn-type valve (10) in a circuit of the Barth type (11). This voltmeter was connected across the centre tap of the filament resistors R 15, R 16 (Fig. 10; pin 5, plug 4) and the ionisation chamber (Fig. 10; pin 4, plug 4).

A potential drop of 20 volts across R 1 (Fig. 12) was obtained, from the 50 volt battery B 1, by adjusting VR 3 with reference to the standard cell.

Fig. 13.



D.C. AMPLIFIER.

R 1	2 x 10^{11}	ohms	R 21	100 k		R 41	24 k	
2	3 x 10^{10}	ohms	22	100 k		42	650 k	
3	3.3 k		23	100 k		43	780 k	
4	2.2 k		24	100 k				
5	470	ohms	25	100	ohms	VR 1	100 k	
6	33	ohms	26	100	ohms	2	50 k	
7	60	k	27	10	k	3	100 k	step
8	100	k	28	100	k	4	25 k	
9	100	k	29	100	k	5	1 M	
10	15	K	30	100	k	6	50 k	
11	15	k	31	100	k			
12	1	M	32	1	M	V 1	EDM20	
13	15	k	33	100	k	2	12SC7	
14	50	k	34	100	k	3	12SC7	
15	100	k	35	330	k	4	12J5	
16	100	k	36	330	k			
17	100	k	37	100	ohms	C 1	30 pF	
18	47	k	38	68	k	2	0.01µF	
19	100	ohms	39	20	k	3	0.01µF	
20	50	k	40	24	k	4	0.01 µF	

M Multi-range voltmeter and electronic recorder.

FIGURE 13.

With S 1 "down", VR 2 was adjusted until M 1 read zero. With S 1 "up", the unknown voltage was applied to the grid of V 1, and the zero reading of M 1 was then restored by backing off the input voltage with the equivalent voltage obtained by adjusting VR 1 and R 1.

The sensitivity of the circuit was such that, near the balance point, 1 scale division of the meter M 1 represented 0.02 volts.

The High Voltage Supplies.

A stabilised 1-2 kilo-volt supply which existed for the original mass spectrometer was connected to a resistor network which gave the variable voltages required for the ion gun.

The Magnet Current Supplies.

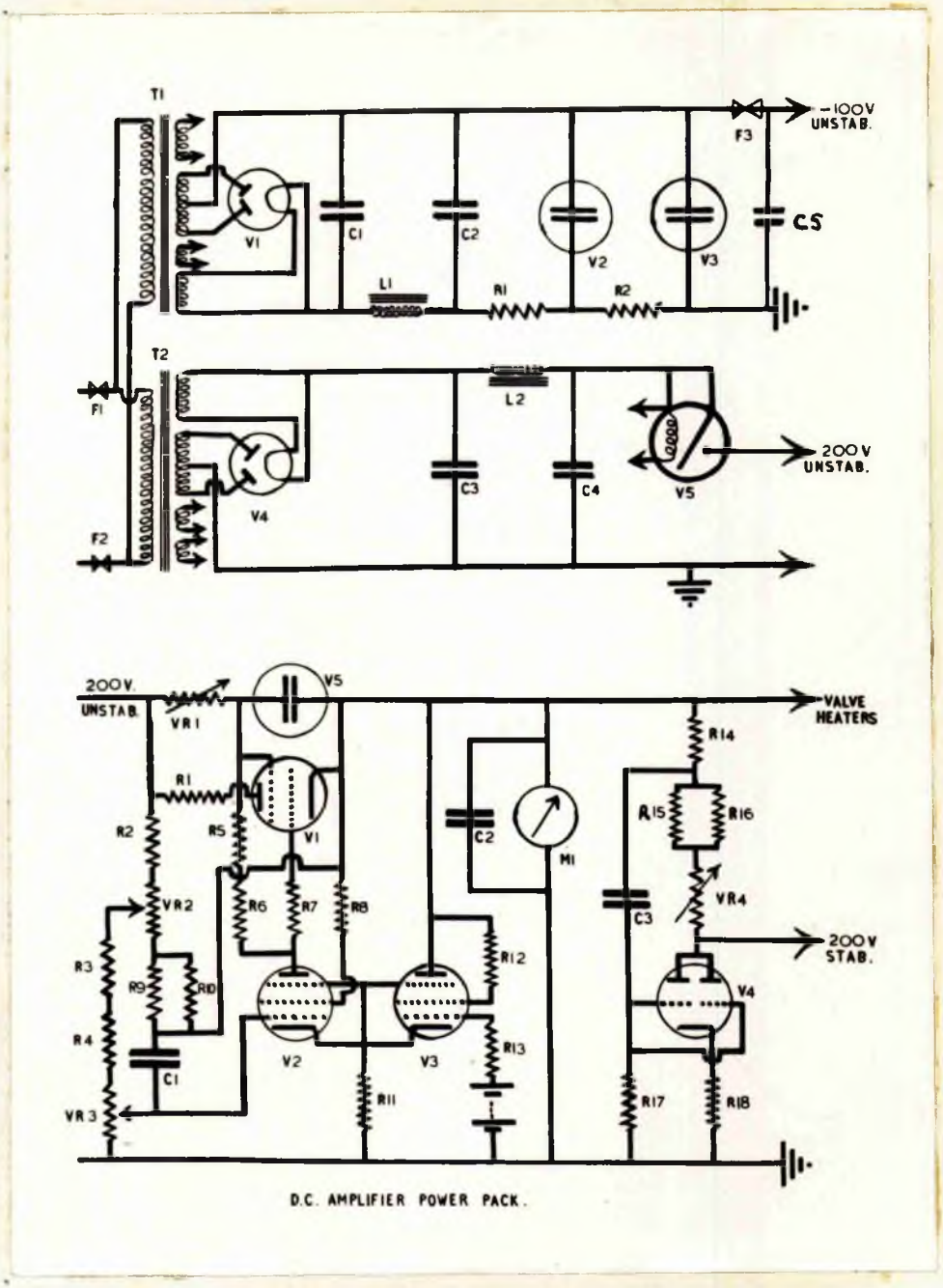
These were obtained from the electronic units built for the original mass spectrometer, and allowed from 4 ma. to 135 ma. D.C. to be fed to the magnet.

The D.C. Amplifier.

The D.C. amplifier, Fig. 13, built from a published design (12), and the mounting at the collector end of the tube unit for the electrometer valve and the associated high resistors were constructed by Naylor (8). The amplifier was double-sided; it employed 100% feedback which gave a voltage gain of unity, and its output was detected by either a robust Simpson Voltmeter or a Honeywell-Brown 5 sec. 0-10 mV. Electronik Recorder, via a suitable automatic range change mechanism.

FIGURE 14.

Fig. 14.



Upper Diagram.

R	1	8.3 k
	2	2.6 k
V	1	5Z4G
	2	VR 150/30
	3	VR 105/30
	4	5U4G
	5	DLS 16
C	1	6 uF
	2	6 uF
	3	4 uF // 4 uF
	4	4 uF // 4 uF
	5	24 uF
L	1	20 H
	2	22 H
F	1	3 amp.
	2	3 amp.
	3	100 mamp.
T	1	350-0-350 v., 150 mamp. 5 v., 3 amp. 6.3 v., 4 amp.
T	2	425-0-425 v., 200 mamp. 5 v., 3 amp. 6.3 v., 3 amp. 6.3 v., 3 amp.

Lower Diagram.

R	1	47 ohms.
	2	550 k
	3	47 k
	4	68 k
	5	68 k
	6	100 ohms
	7	100 ohms
	8	120 k
	9	10 k
	10	10 k
	11	10 k
R	12	120 k
	13	1.4 M
	14	47 ohms
	15	1 k
	16	1 k
	17	2 M
	18	300 ohms
C	1	0.5 uF
	2	1 uF
	3	2 uF
VR	1	5 k
	2	5 k
	3	50 k
	4	500 ohms
V	1	12 E 1
	2	EF 37 A
	3	EF 37 A
	4	12 SC 7
	5	VR 105/30
M	1	300 volts

The power required for this D.C. amplifier was supplied from the circuits shown in Fig. 14.

The performance of this amplifier has been discussed by Hamer and Naylor.

EXPERIMENTAL WORK WITH THE MASS SPECTROMETER.

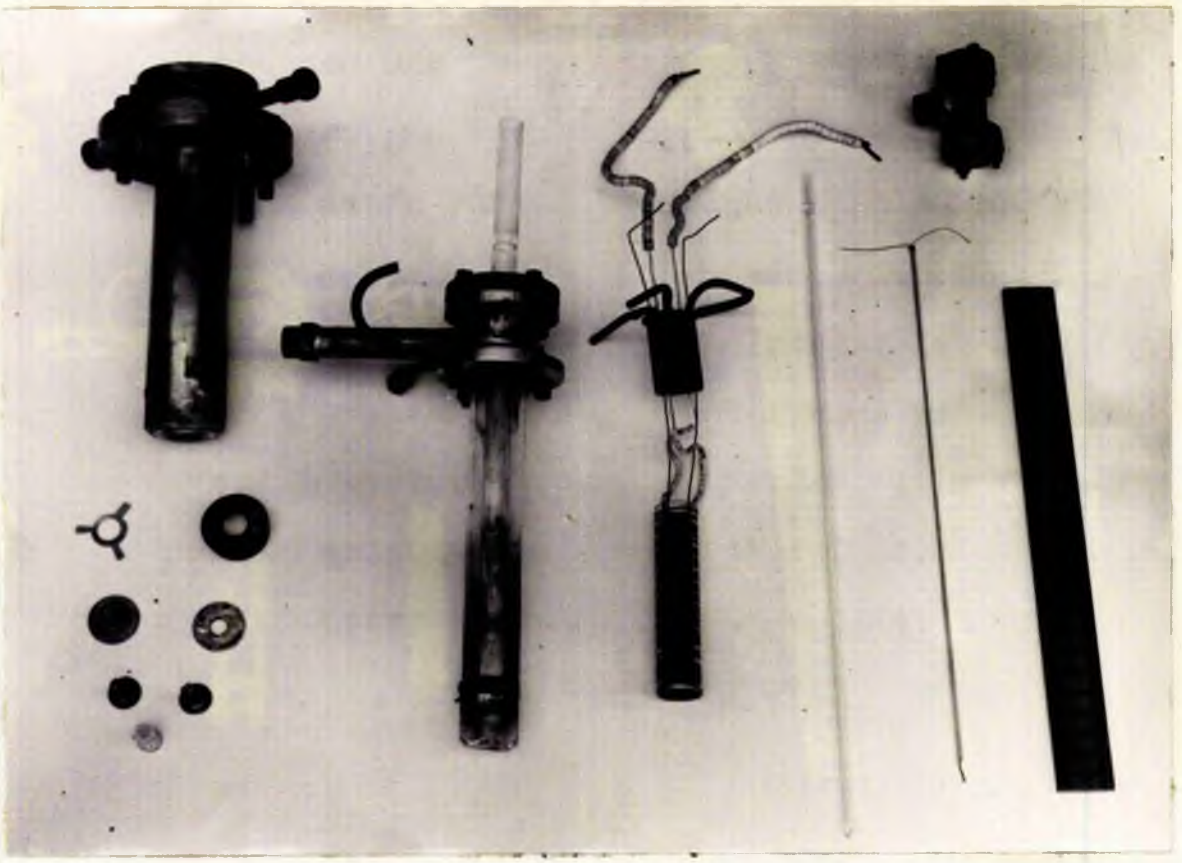
The initial operation and behaviour of the completed mass spectrometer for the determination of the appearance potentials of ions from some aromatic molecules and the ionisation potential of the benzyl radical have been described elsewhere (6).

During this work, contamination and subsequent malfunctioning of the ion source was occurring and the trouble was traced to the vapour from the oil diffusion pumps. This oil vapour was also responsible for the considerable background spectra which were obtained. It was not possible to continue the ionisation investigations in the presence of such contamination, and these oil pumps were replaced by mercury diffusion pumps (Type 2M3, Messrs Edwards (Ldn) Ltd.), which gave much cleaner background spectra displaying only the mercury isotopes in the mass/charge regions 200, 100 and 68 units; the peaks in the latter region occurred only at the highest electron energies.

The original plans for a mass spectrometric investigation of the pyrolysis of mercury dibenzyl were at this stage upset by the discovery, reported in Part 2 of this Thesis, that this compound had a vey low vapour pressure at 50°C., and that at temperatures above 100°C. the solid decomposed readily, even

FIGURE 15.

Fig. 15.



The components of the reactor furnace.

in a vacuum. From such observations it was realised that useful gas-phase kinetic data could not be obtained from this compound, even with the assistance of the mass spectrometer, and the author's attention, at that time, was restricted to the construction of a reactor furnace, shown in Fig. 15, which was used in an unsuccessful attempt, discussed by Hamer (6), to detect benzyl radicals formed during the thermal decomposition of benzyl iodide.

At this stage, attention was therefore diverted to perfecting methods for thermally decomposing mercury dibenzyl in solution in various solvents, as reported in Part 2 of this Thesis.

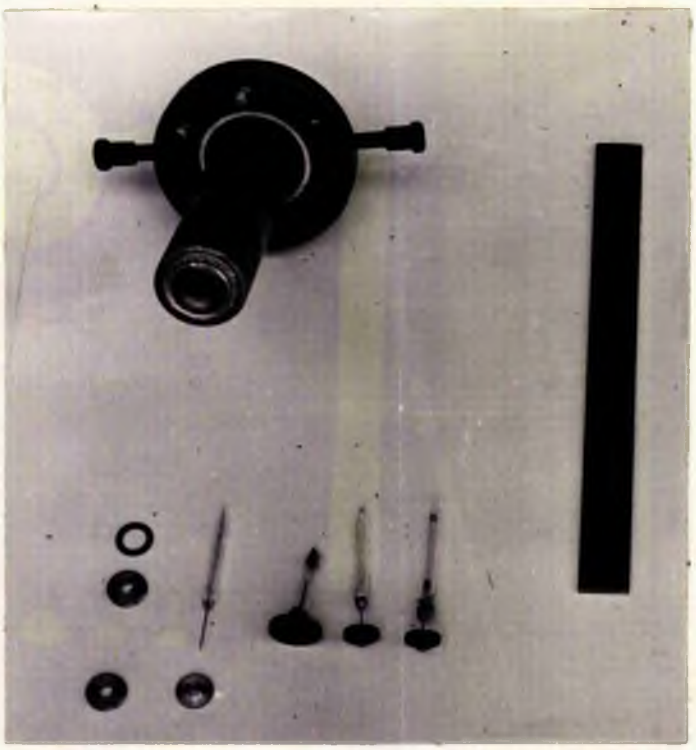
ATTEMPTS TO MEASURE THE VAPOUR PRESSURE OF MERCURY DIBENZYL USING THE MASS SPECTROMETER.

Before commencing kinetic work with mercury dibenzyl, some attempts were made to measure the vapour pressure of this material by gas saturation techniques, as outlined in Part 2.

The results obtained indicated that the substance decomposed readily and had a very low vapour pressure at moderate temperatures. The data were of a low order of accuracy, and it was considered that the use of the mass spectrometer to follow the temperature dependence of the intensity of the beam of parent ions $HgBz_2^+$, produced from the vapour of the material escaping through a fine leak into the mass spectrometer, might provide more accurate information over an extended temperature range, and might indicate more clearly the onset of extensive

FIGURE 16.

Fig. 16.



Some of the effusion vessels,
and the water jacket.

decomposition in the material. Such techniques to measure very low vapour pressures have been utilised by Tickner and Lossing (13).

Some initial experiments were performed using effusion vessels of the type shown in Fig. 16, each of which was constructed from a C 40 glass tube sealed at one end to a fine stainless steel tube approximately 1½" long and 0.0135" internal diameter. Each tube was silver soldered into a hole drilled in a circular brass plate which could be sealed with a Gaco 'O' ring into the lower end of the water jacket which had been designed for the reaction furnace of the mass spectrometer. The end of the steel tube projected slightly below the brass plate, and it was thus placed centrally over the hole in the top plate of the ionisation chamber of the mass spectrometer.

Mercury dibenzyl was added to a vessel, and the glass tube sealed at its upper end. The vessel was then inserted in the water jacket which was then assembled into the mass spectrometer. The volume above the effusion vessel was filled with water which could be stirred by a fine stream of air bubbles from a compressor, and water from a thermostat was circulated through the water jacket.

Scans over the mass region 200-400 units, with the effusion vessel at room temperature, showed only a group of peaks in the approximate mass region 380 units, judged by the ion accelerating voltage and magnet current settings, allowing

for possible magnetic hysteresis effects.

Attempts to assign accurate mass/charge values to these peaks led to the conclusion that the mass region 400 was being observed. The mass assignments were made in the following manner.

The mercury isotopes at 198-204 mass units formed a well-recognised background in the mass spectrometer, and were brought into focus with 1600 volts applied to the ion gun, using a magnet current in the region 120-130 ma. The instrument was focussed to collect the singly-charged mercury isotope ions of mass 200 units. The ion accelerating voltage was then reduced to 800 volts, and this operation brought the peaks of suspect mass into focus.

From equation (3) of the simple theory presented on page 4. it is seen that at constant field strength the mass of the ions collected is inversely proportional to the ion accelerating voltage, V. Thus it was concluded that mass 400 units, to within an estimated error of ± 6 mass units, was focussed by this operation.

A prolonged search under various conditions revealed no ions in the mass region 205-382 units, even with hot water surrounding the effusion vessel, and it was concluded that mercury dibenzyl gave neither the parent ion $HgBz_2^+$, nor ions of the type $HgBz^+$ in appreciable concentration under the conditions employed during these experiments. Because of the absence of the parent ion, the measurements of the vapour

pressure of mercury dibenzyl by this method were not developed beyond this initial stage. Had further experiments been desirable, conditions would have been arranged to ensure the molecular flow of vapour through the capillary tube or through some other form of leak (14).

A brief investigation of the peaks in the 400 mass region revealed that there were six broad, overlapping peaks, with a pronounced tail on the side of lower mass. The hypothesis that they were produced by the dimeric ion Hg_2^+ would have been untenable because, if such were the case, there would have been 12 peaks produced from the six common isotopes of mercury extending over the mass range 396-408 units, i.e. a range of 13 mass units.

By electrostatic scanning, a change of 35 volts in the ion accelerating voltage was required to cover the 7 mass units 198-204 in the normal mercury mass spectrum. A corresponding change of 40 volts, or the equivalent of 8 mass units, was required to cover the peaks in the 400 mass region.

Peaks of similar shape in the mass region 400 units could be obtained with the other mass spectrometer available in the Chemistry Department, when this instrument was operated without its CO_2 cold trap, thus producing a relatively high pressure of mercury vapour in the tube.

Similar effects, which involved mercury ions giving traces corresponding to ions of double the mass of the normal ions, were observed by Thomson (15), who ascribed the phenomenon to

diatomic mercury. Mattauch and Lichtblau observed a similar effect with gases at high pressures in a mass spectrometer, and traced the occurrence to ions which had initially a double charge losing one charge after the acceleration region and before the magnetic deflection region of the mass spectrometer. Thus, these singly charged ions entered the magnetic field with twice the energy corresponding to the single charge by which they are deflected, thus being equivalent to ions of single charge and double mass.

Norton (16) observed such "double mass" peaks with argon at 80 mass units, with mercury which showed 6 peaks at 396-408 mass units, and with other gases except hydrogen and deuterium. He published scans showing the tailing observed with such peaks, attributed by Mattauch to magnetic fringing effects. The argon peak at 80 mass units occurred only when the energy of the ionising electrons was greater than the second ionisation potential of argon, and the intensity of the peak at 80 mass units followed that of the A^{++} peak at 20 mass units.

There is considerable spectroscopic evidence for the existence of a dimer Hg_2, which has a bond dissociation energy of 1.4 kcal./mole (17) or 3.2 kcal./mole (18), but similar evidence for an ion Hg_2^+ is less conclusive (17).

Thus, it may be stated that the number and shape of the peaks obtained in the mass region 400 units with the injection of mercury or mercury dibenzyl into the mass spectrometers agrees with the suggestion that they are caused by the simple

ions Hg^{+} which possess twice the energy expected because of their previous double charge.

PART 2.

THE THERMAL DECOMPOSITION OF MERCURY DIBENZYL.

THE THERMAL DECOMPOSITION OF MERCURY DIBENZYL.

Previous Work Concerning the Decomposition of Mercury Dibenzyl.

There appeared to be little kinetic work recorded in the literature which concerned the pyrolysis or thermal decomposition of mercury dibenzyl. The following information was, however, relevant to the investigations which it was intended to undertake.

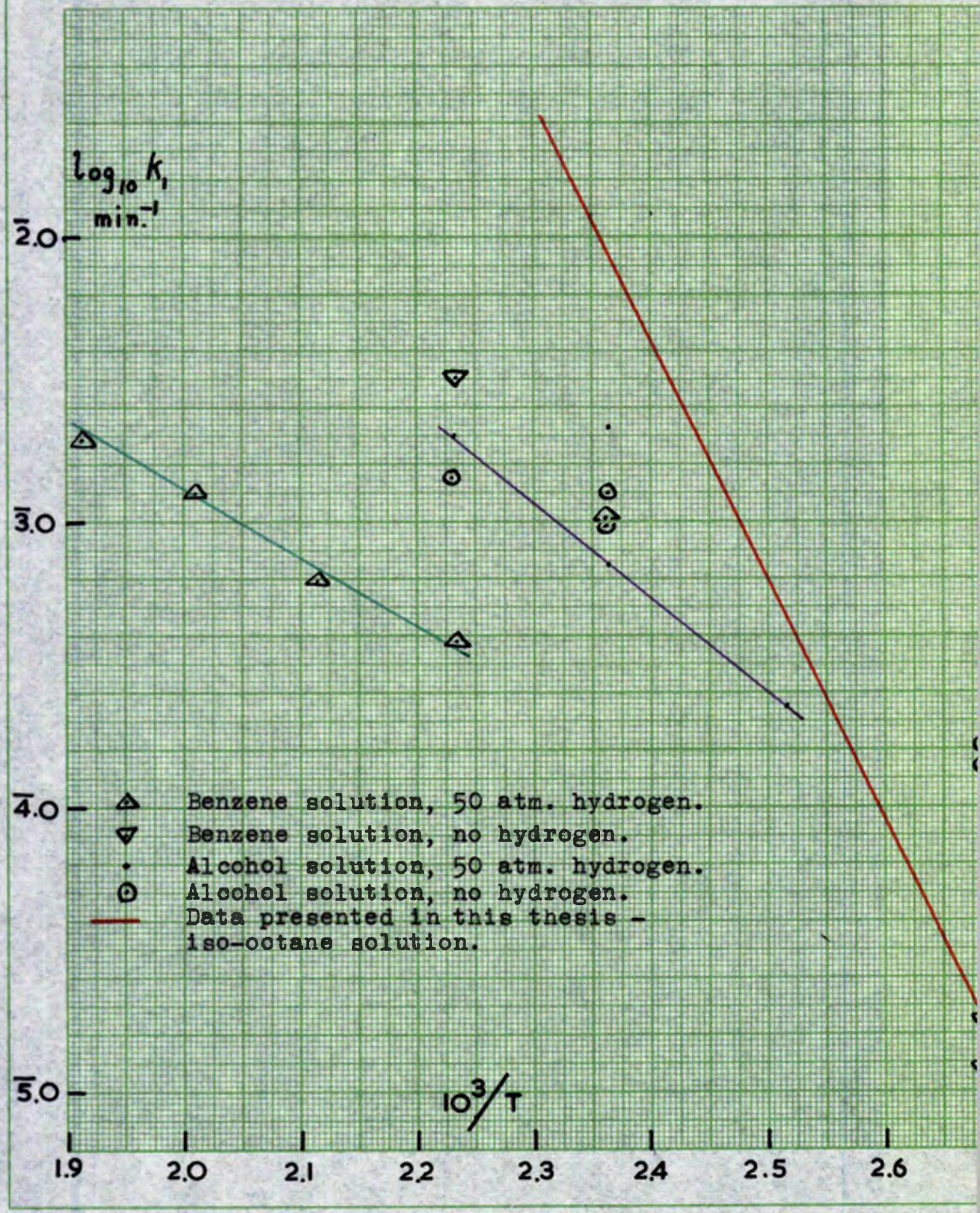
Pope and Gibson (19) found that mercury dibenzyl (which gave correct analyses but which had a low m.pt.) when heated to 170°C. with phosphenyl chloride decomposed to mercury and dibenzyl: they were thus unable to prepare the expected phenyl benzyl chlorophosphine.

Wolff (20) observed that when mercury dibenzyl was heated (presumably in air) to a temperature above its melting point it decomposed easily to mercury and dibenzyl. Banus (21) reported that mercury dibenzyl was, however, stable in sunlight.

Hein and Wagler (22) found that the molecular weight of mercury dibenzyl, determined in alcohol by the ebullioscopic method, was 461, 434 and 466, instead of the calculated value 382.8 .

Nasuwajew and Koton (23) described the thermal decomposition of mercury dibenzyl in solution in both benzene and alcohol, with and without 50 atmospheres of hydrogen. Mercury and dibenzyl were the only products observed. They found that "the quantity of mercury precipitated altered comparatively little at one and the same temperature when the reaction was carried out in benzene or alcohol, with or without (hydrogen) pressure."

Graph 1. Plots of the data of Rasuwajew and Koton.



An analysis of their data showed linear plots for $\log_{10} k_1$ against $1/T^{\circ}A.$ for the decompositions in alcohol and benzene in the presence of 50 atmospheres of hydrogen, with energy of activation values of 15.0 kcal./mole and 9.9 kcal./mole respectively. Their data for the decomposition in the absence of hydrogen were less reliable and no linear plots could be constructed. Graph 1 shows these observations.

Rasuwajew and Koton (24) also found that solid mercury dibenzyl was catalytically decomposed by various finely divided metals (Pd, Pt, Ag, Au, Cu, Ni, Fe, Co in decreasing order of activity), and they concluded that the decomposition could be represented by the equation

$$Bz\text{-}Hg\text{-}Bz \longrightarrow Bz_2 + Hg ,$$

both with and without 30 atmospheres of hydrogen, over the temperature range 25°C. to 75°C.

These authors later suggested (25) that the compound decomposed to give radicals which dimerised on the surface of the catalyst.

This observation was confirmed by Nesmeyanov (26) who isolated dibenzyl from the decomposition of mercury dibenzyl at 175°C. in the presence of 50 mm. of hydrogen. The same product, together with mercuric sulphide, occurred when mercury dibenzyl was heated with sulphur (27).

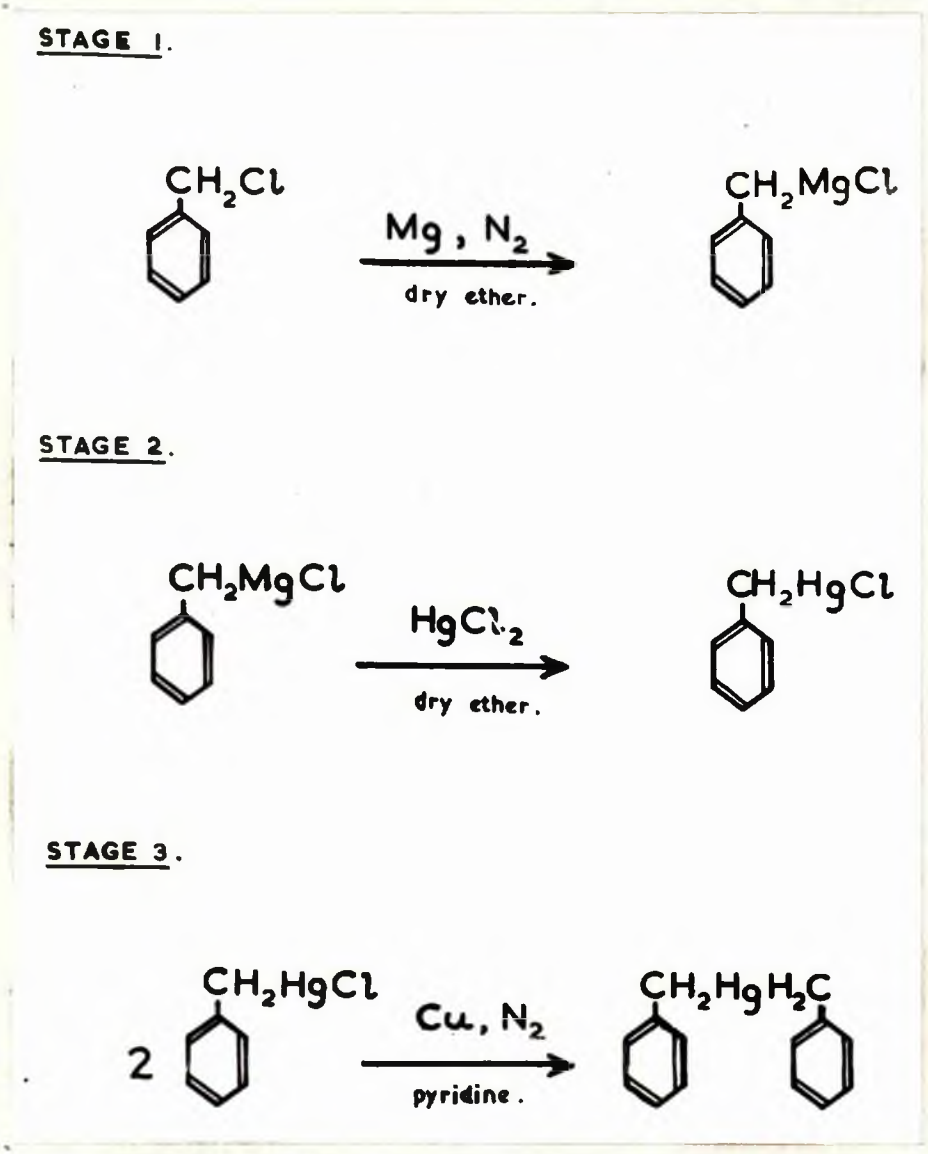
Photochemical decompositions of mercury dibenzyl dissolved in methanol gave high yields of dibenzyl and mercury (28), (29).

With added methyl iodide, the products were mercuric iodide, dibenzyl, methane and formaldehyde (30). The decomposition in benzene as solvent, with added methyl iodide, yielded mercuric iodide, dibenzyl and ethane (30).

A direct indication that radicals are produced during the decomposition of mercury dibenzyl was supplied by Koton (31), who was able to accelerate the polymerisation of vinyl acetate with added mercury dibenzyl, or other organo-metallic compounds.

FIGURE 17.

Fig. 17.



The preparation of mercury dibenzyl.

The Preparation of the Mercury Dibenzyl.

Mercury dibenzyl was prepared by the following method :-

STAGE 1. A stream of oxygen-free, dry nitrogen excluded air and moisture from a reflux apparatus which contained sodium-dried ether and magnesium turnings. A solution of freshly distilled benzyl chloride (b.pt. 178-179°C.) in sodium-dried ether was added at such a rate that the ether refluxed gently. After this addition, the ether was refluxed for two hours to complete the reaction. (See Fig. 17).

STAGE 2. The filtered Grignard solution from Stage 1 was added dropwise, under an atmosphere of oxygen-free, dry nitrogen, to a vigorously stirred slurry of finely divided, dry mercuric chloride in sodium-dried ether (32). A precipitate of benzyl mercury chloride formed. After the addition, the ether was refluxed for two hours, with continued stirring. (In subsequent preparations, the filtered Grignard solution from Stage 1 was refluxed in a Soxhlet apparatus whose extraction thimble contained the finely divided mercuric chloride (33)).

The reaction mixture was treated with water, and the ether distilled off. Dilute hydrochloric acid was added to the aqueous suspension to remove the complex salts, and the crude benzyl mercury chloride was filtered off and dried.

A small portion of this product was recrystallised from absolute ethyl alcohol and dried. M.pt. 103-104°C. (uncorrected). (Literature value 104°C. (20)). The yield of the crude, dry intermediate was 40.8 gm. (79% from 20 gm. of benzyl chloride).

STAGE 3. Oxygen-free, dry nitrogen was passed through dry pyridine. Benzyl mercury chloride was added and when it had dissolved copper-bronze was added and the mixture was agitated (22). A green colour developed. The mixture was warmed slightly, and allowed to stand for 10 minutes. Many crystals were formed in the reaction mixture. As a result of several preparations, it is considered that the following method gives the most satisfactory recovery of the desired product. The semi-solid mixture was treated with 2 N. sulphuric acid until no further precipitation occurred. The solids were filtered off, and the product was extracted with portions of hot chloroform. The combined chloroform solutions were washed twice with 2 N. sulphuric acid, twice with 2 N. ammonia solution, twice with distilled water and were then dried with anhydrous sodium sulphate. The volume of the solution was reduced by evaporation to the point of crystallisation, charcoal was added to decolourise the light brown liquid and filtered off, and the chloroform was evaporated from the colourless filtrate. The solid obtained was twice recrystallised from ethyl acetate, and then vacuum dried. The m.pt. of the white needle crystals was 111-113.5°C.$^{\phi}$ (uncorrected). (Literature value 111°C. (20)). The preparation yielded 11.7 gm. of mercury dibenzyl. (49% from 40.8 gm. of benzyl mercury chloride).

This stock mercury dibenzyl was stored in a brown bottle which was kept in darkness.

ϕ 108.7-111.1°C. (corrected).

The Analysis of the Mercury Dibenzyl.

It is usually desirable that the materials used for kinetic studies should be of the highest possible purity. During the kinetic work, the purity of the stock mercury dibenzyl was investigated by several methods.

(1) The Carius method of analysis.

Two analyses were attempted by reacting the stock mercury dibenzyl with 3.4 ml. of concentrated nitric acid in a sealed tube (34). The tube and contents were heated to 200°C. over a period of 3 hours. The addition of a slight excess of sodium hydroxide to the reaction mixture precipitated mercuric oxide which was dissolved by the addition of potassium cyanide, and the solution was then saturated with hydrogen sulphide. Ammonium acetate was added and the solution was boiled to expel the ammonia. The precipitated mercuric sulphide was collected, washed with water, hot dilute hydrochloric acid and hot water, and then dried and weighed. This washing was repeated until no further loss in weight occurred.

0.1595 gm. mercury dibenzyl yielded 0.1036 gm. mercuric sulphide, or 107% of the theoretical quantity.

The second Carius tube fragmented on opening.

(2) Oxidations with nitric acid.

A standard solution of mercuric nitrate was prepared by dissolving a known weight of mercury in refluxing concentrated nitric acid. The resultant solution was cooled and diluted to a standard volume. The solution was analysed by the ammonium

thiocyanate and sodium chloride methods (35).

Calculated normality of the mercuric nitrate 0.121(3) N.

Normality found (ammonium thiocyanate method) 0.120(4) N.

Normality found (sodium chloride method) 0.120(1) N.

Thus, with the standard mercuric nitrate solution, these analytical techniques were satisfactory.

Mercury dibenzyl was oxidised with diluted nitric acid under reflux for the times noted. The resultant solutions were diluted to standard volumes, and aliquots were titrated with 0.1166 N. ammonium thiocyanate solution, using ferric alum as indicator.

gm. mercury dibenzyl	ml. conc. nitric acid	ml. distilled water.	reflux hours	% Hg recovered
0.4895	3.5	7	1	84
0.2578	3.2	4	1	88
0.2770	7.1	4	1½	92
0.2865	4.5	4	12¼	84

(3) <u>Oxidations with nitric acid mixed with acetic acid</u>.

Wolff (20) had observed that mercury dibenzyl was decomposed by acetic acid when the mixture was heated to 170°C., giving mercury, toluene, benzyl acetate and dibenzyl as products.

Mercury dibenzyl was refluxed with a mixture of glacial acetic acid (to decompose the mercury dibenzyl) and ANALAR nitric acid (to oxidise the mercury produced) and the reaction mixture was analysed by the precipitation technique outlined above for the Carius method. The results for several such

experiments are quoted in the Table below.

gm. mercury dibenzyl	ml. glacial acetic acid	ml. conc. nitric acid	hours reflux	% Hg recovered
0.2098 s	5.9	4.0	5¼	98.4
0.1744 s	6.2	5.2	4½	97.6
0.1996 s	6.2	6.1	3½	99.4
0.1256 r	6.2	4.8	4¼	92.8
0.1262 r	5.9	4.6	5	100.3
0.1416 r	5.9	5.1	4	100.7
0.1332 r	5.9	4.1	3	93.2
0.1387 r	6.4	4.9	2	97.3

s indicates stock mercury dibenzyl, see page 30.
r indicates mercury dibenzyl which had been recrystallised from iso-octane under vacuum conditions, see page 58.

(4) <u>The iodine method of analysis</u>.

In the presence of water and potassium iodide, the stock mercury dibenzyl was reacted for 4 hours with an excess of iodine using chloroform, which was under reflux, as a solvent. This method of analysis has been described by Whitmore and Sobatzki (36).

The results obtained with less than 2 hours reflux indicated that the reaction

$$HgR_2 + 2\ I_2 \longrightarrow HgI_2 + 2\ RI$$

was incomplete.

The excess iodine was back-titrated with thiosulphate solution which had been standardised by three independant determinations with Analar potassium iodate. The results are indicated in the Table overleaf.

20.00 ml. iodine solution were equivalent to 20.10 ml. of 0.0995 N thiosulphate solution.			
Gm. of sample refluxed with 20.00 ml. I_2	ml. thio. reqd. for excess I_2	thio. equiv. to I_2 used by sample	% purity
0.1148 0.1129 0.1184	8.10 8.30 7.60	12.0 11.8 12.5	99.5 99.5 100.5

This method for the analysis of organic compounds of mercury can be recommended as simple and accurate. It would be capable of a precision greater than that attained in these experiments by suitable adjustment of the concentrations of the reagents employed. This was attempted for the later analyses performed on p-chlorbenzyl mercury chloride and mercury di-(p-chlorbenzyl) as reported on pages 87 and 90.

(5) <u>The gravimetric method of analysis</u>.

Experiments were performed to identify the products of the thermal decomposition of mercury dibenzyl dissolved in iso-octane. For reasonable precision, relatively large quantities of the stock mercury dibenzyl were sealed in small glass vessels, in the absence of air, with 1.02 ml. degassed iso-octane, using the proceedure described on page 61.

The sealed vessels were inserted in a thermostat at 131°C., at which temperature complete solution of the reactant was rapidly attained. After the heating period, which was sufficiently long to ensure complete decomposition, the solutions in the vessels remained perfectly clear when cooled

to room temperature; there was also a globule of mercury in each vessel.

Each vessel was opened, the iso-octane solution of the products was diluted, and the u-v absorption spectrum was obtained. The only solute detected was dibenzyl. (For a discussion of the identification of the dibenzyl, see page 69).

Subsequently, the quantity of mercury in each vessel was determined by filtering the mercury into a No. 4 sintered-glass Gooch crucible, and washing the mercury and the disc carefully with iso-octane. Each crucible was then dried in air to a constant weight.

Recovery of mercury from mercury dibenzyl.

Experiment No.	gm. mercury dibenzyl	gm. mercury recovered	% mercury recovered
11/I	0.1457	0.0763	99.8
12/I	0.4048	0.2138	100.8

These experimental results indicated that the stock mercury dibenzyl was reasonably pure material.

This gravimetric method of analysis is now regarded as the most accurate of the five procedures described.

The purity of the stock mercury dibenzyl was again considered as a result of observations made during Experiments 9-10/I, 13/I and 14/I which are described on pages 56 and 74.

As a result of these experiments, the mercury dibenzyl was recrystallised from iso-octane under vacuum conditions. A gravimetric analysis of 0.11334 gm. of this vacuum recrystallised material gave 0.05955 gm. mercury, or 100.2% of the theoretical quantity.

THE VAPOUR PRESSURE OF MERCURY DIBENZYL.

(a) Thermal Stability Experiments.

An initial experiment was performed to assess the thermal stability of the stock mercury dibenzyl.

Four ampoules containing the solid mercury dibenzyl were evacuated to better than 10^{-5}mm. and then sealed.

Each vessel was then inserted for 20 minutes in a liquid boiling under reflux. At the end of this period, each vessel was cooled, opened, and the m.pts. of samples of the residual materials were determined.

Temp. of bath, °C.	Appearance of product	Uncorrected m.pt. of products, °C.
unheated	white	113°
100°	slightly grey	112-113° ø
107°	slightly grey	113°
118.6°	light grey	111.5-112°
ø uncorrected m.pt. of the pure material on the same slide at the same time :- 113°C.		

Thus, it was concluded that prolonged heating of mercury dibenzyl in a vacuum at temperatures above 107°C. caused some decomposition to occur. As a result of this work, during the subsequent experiments to determine the vapour pressure of mercury dibenzyl the material was not heated to temperatures above 100°C.

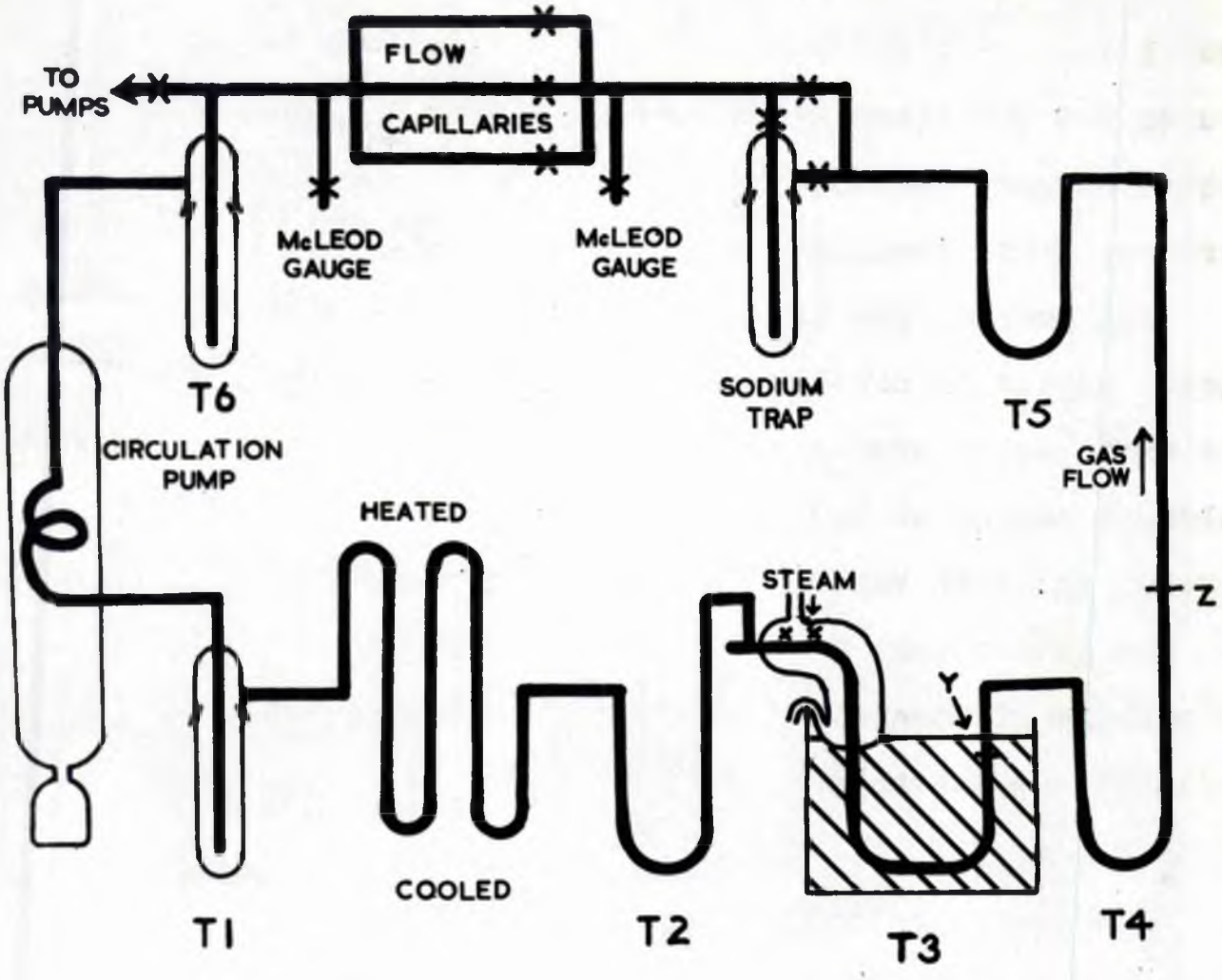
(b) The Apparatus used for the Vapour Pressure Experiments.

The vapour pressure of mercury dibenzyl was obtained by a gas saturation technique.

Dry oxygen-free nitrogen was circulated round the closed system shown in Fig. 18.

FIGURE 18.

Fig. 18.



A diagram of the apparatus used for the vapour pressure experiments.

The nitrogen, circulated by the pump at pressures of from 1 to 9 mm., was freed from mercury vapour from the McLeod gauges and the circulation pump by a trap T 1 cooled with liquid oxygen, followed by a device to separate colloidal mercury. This consisted of alternate heated and cooled U tubes.

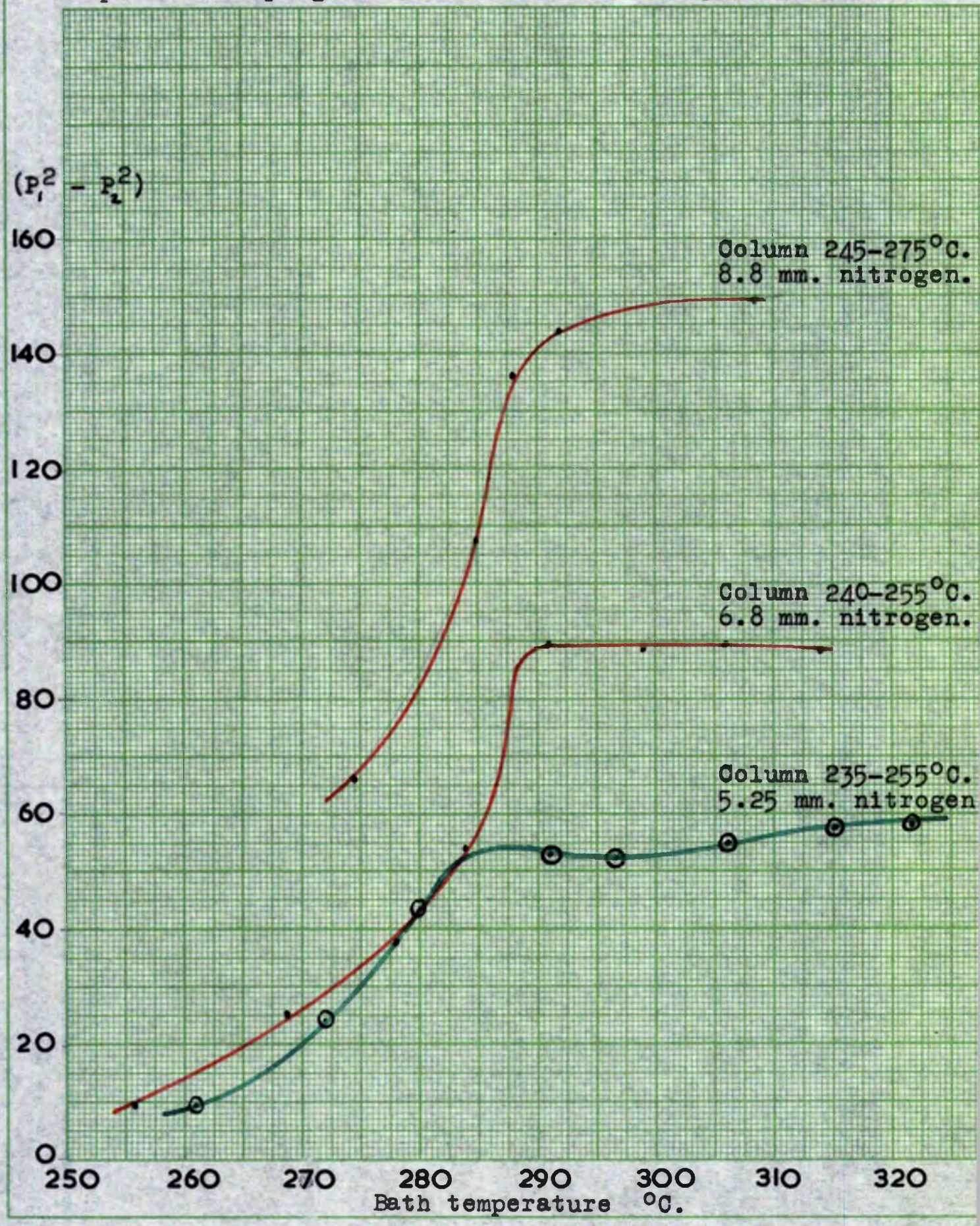
The carrier gas then passed through a trap T 2 cooled with liquid oxygen to prevent back diffusion of mercury dibenzyl, and was next passed over a boat, at position XX, containing mercury dibenzyl heated to 100°C. by a steam jacket. Saturation of the carrier gas with vapour from the solid was attained by passing the gas into a trap T 3 held at approximately 50°C. by an accurately thermostatted water-bath. That saturation had been achieved was determined by the presence of a crystalline deposit in this trap T 3.

The emerging gas, now saturated with mercury dibenzyl vapour at the temperature of the bath, was passed into a collection trap T 4 cooled with liquid oxygen, at which temperature almost all the mercury dibenzyl vapour was removed.

Back diffusion of mercury and sodium vapours from the McLeod gauges and the heated sodium trap into the collection trap T 4 was prevented by a trap T 5 cooled with liquid oxygen.

The carrier gas was returned to the circulation pump via a heated trap containing sodium which removed any oxygen, and then through a suitable flow capillary, on each side of which was a McLeod gauge, and finally through another trap T 6 cooled with liquid oxygen.

Graph 2. Pumping characteristics of the apparatus.



(c) Calibration of the Apparatus.

It is known that the pumping stability, at a given gas pressure, of the usual type of mercury circulation pump is affected by the pump bath temperature and the pump column temperature. To select the optimum operating conditions, calibration experiments were performed with the completed apparatus, operating under conditions similar to those used during the subsequent vapour pressure experiments.

The pump bath temperature, which could be controlled to $\pm 1^{\circ}$. by a Sunvic energy regulator, was measured by a thermometer immersed in the solder bath. The pump column temperature was controlled by an electrical heating tape across which various voltages could be applied. This temperature was recorded by a thermometer fixed in the column lagging.

Nitrogen was circulated through the apparatus, using various initial static pressures from 5 to 9 mm., with the traps heated or cooled as described for an experiment below. When thermal stability had been attained the pressure drop across the flow capillary was measured at 2 minute intervals during a period of 20 minutes, together with the steady bath and column temperatures. The bath or column temperature was then adjusted and a further set of readings obtained.

The type of results obtained are illustrated in Graph 2. These indicated that for reasonable pumping stability, the optimum bath temperature would be about 300°C., with a column temperature of approximately 240°C.

(d) Description of an Experiment.

Mercury dibenzyl was inserted into the boat and placed at position XX in the apparatus. All traps were heated or cooled as described above, with the exceptions that the saturator trap T 3 was cooled with liquid oxygen and the collector trap T 4 was at room temperature. The apparatus was then evacuated. A suitable amount of nitrogen carrier gas was admitted from the reservoir, and then the circulation-pump bath and column temperatures were adjusted for maximum stability of pumping, in accordance with the data previously obtained for the system. The carrier gas was then circulated for 1 hour over the heated sodium.

Steam was then passed through the jacket. When a steady jacket temperature had been reached, a vapour pressure determination was started by replacing the liquid oxygen cooling on the saturator trap T 3 by a thermostat, and cooling the collector trap T 4 with liquid oxygen. During the course of a determination the McLeod gauge pressures and the circulation-pump bath and column temperatures were measured at intervals of five minutes.

To end a determination, the saturator trap T 3 was cooled with liquid oxygen, the steam jacket and sodium trap were allowed to cool and air was admitted cautiously to the apparatus. (Rapid admission of air blew mercury dibenzyl solid from the boat all round the apparatus). The collector trap T 4 was cut off at the points Y and Z, and the crystalline deposits

were dissolved in chloroform and the solution placed in a graduated flask. The trap was then carefully washed several times with chloroform and these washings were added to the solution. The volume of the solution was made up to the graduated mark and the ultra-violet absorption spectrum of the solution determined using a silica cell of path length 1 cm., against the solvent in a similar cell as standard.

(e) Calculations from the Data.

Assuming that no decomposition had occurred during an experiment, the vapour pressure of mercury dibenzyl could be calculated from the relationship :-

$$\frac{\text{moles } N_2 \text{ passed per unit time}}{\text{moles M.D.B. passed per unit time}} = \frac{\text{partial pressure of } N_2}{\text{partial pressure of M.D.B.}}$$

The number of moles of nitrogen flowing per unit time were determined by the use of Meyer's modification of the Poiseuille formula :-

$$\text{Rate of flow} = \frac{\pi r^4 (p_1^2 - p_2^2)}{16 \eta l RT} \text{ moles/second.}$$

$$= K(p_1^2 - p_2^2) = K\Delta(p^2) \text{ moles/second.}$$

in which
- r radius of capillary in cms.
- l length of capillary in cms.
- p_1 pressure before the capillary.
- p_2 pressure after the capillary.
- η viscosity of nitrogen in poises at temperature T°A.
- R the gas constant.
- T temperature in °A.

The number of moles of mercury dibenzyl collected during an experiment were determined by ultra-violet absorption

TABLE 2

and

TABLE 3.

Table 2.

The Vapour Pressure of Mercury Dibenzyl.

Expt. No.	$\Delta(p^2)$ mm.^{2}	Duration of collection, minutes.	Saturator °C.	$HgBz_2$ collected moles x 10^7	vapour pressure mm. x 10^3
1	39.4	5	100	14.5	8.7
2	27.5	20	68-72	8.5	1.4
3	32.2	20	75	17.7	2.7
4	19.9	60	50.4	1.6	0.3
5	65.3	51	50.4	4.5	0.6
6	22.7	60	51.5	-	-
7	9.2	74	50.1	3.8	1.1
8	9.3	60	49.9	5.6	1.6
9	13.4	60	50.6	7.9	1.9
10	32.2	60	52.2	4.9	0.7
11	3.4	60	50.1	1.3	0.6

Notes. (a) Capillary constants Expts. 1-3 1.06×10^{-6} (N_2, 0°C., p in mm.)

Expts. 4-11 3.26×10^{-8} (N_2, 20°C., p in mm.)

(b) Experiments 1-3 were performed with a simpler form of apparatus than that illustrated in Fig. 18.

Table 3.

The Corrected Vapour Pressure of Mercury Dibenzyl.

Expt. No.	$HgBz_2$ collected moles x 10^7	vapour pressure mm. x 10^4
5	4.0	0.5
9	4.3	1.0

analyses of the chloroform solutions of the solid products. Chloroform solutions of mercury dibenzyl were shown to obey Beer's Law accurately.

Although of a low order of accuracy, the data given in Table 2 indicates that mercury dibenzyl is a somewhat involatile compound.

The vapour pressure data given in Table 2 were calculated on the assumption that only mercury dibenzyl was present in the chloroform solutions which were analysed. In fact, the absorption spectra of these solutions indicated the presence of material(s) other than mercury dibenzyl, and this suggested that decomposition of the mercury dibenzyl had occurred during these experiments. The shapes of the absorption curves for the products suggested that dibenzyl was present.

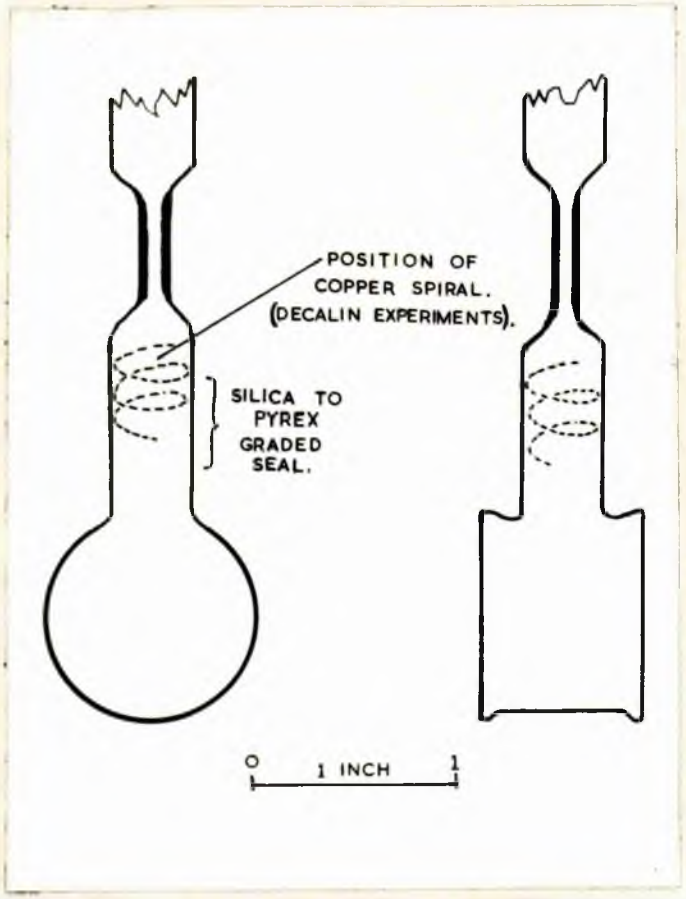
From the absorption spectrum of a standard solution of dibenzyl in chloroform, which was shown to obey Beer's Law accurately at the wavelengths of interest, together with the absorption curve for mercury dibenzyl in the same solvent, it was possible to calculate the concentration of mercury dibenzyl in the solutions of the products from the collector trap T 4, assuming that these two substances were the only materials which contributed to the optical absorption over the regions of the spectra on which the analyses were based. The vapour pressure of mercury dibenzyl, calculated after making due allowance for the presence of dibenzyl in the products, is given in Table 3.

As a result of these vapour pressure experiments, it was now apparent that the mercury dibenzyl was neither a sufficiently volatile nor a sufficiently stable material for any useful conventional kinetic work in the gas phase to be readily performed. The ready decomposition of the material at moderate temperatures prevented the attainment of higher partial pressures and the available pressures of 10^{-3} to 10^{-4} mm. were too low to be used.

Later, unsuccessful attempts were made to obtain the temperature dependence of the vapour pressure of mercury dibenzyl using the mass spectrometer. These experiments have been described above.

FIGURE 19.

Fig. 19.



A diagram of the silica reaction cell used during the experiments with n-hexane and decalin. When the copper spiral was in use the cell was inverted for the period of the reaction.

THE THERMAL DECOMPOSITION OF MERCURY DIBENZYL IN SOLUTION.

Since the gas phase decomposition of mercury dibenzyl could not be pursued the possibility of studying the decomposition in solution was considered. It seemed probable that free benzyl radicals would be produced and in order to simplify the kinetics it was clearly desirable that the solvent should not be attacked by these radicals. This suggested saturated hydrocarbons as solvents since the stable benzyl radicals would not be able to abstract hydrogen atoms from such materials at the temperatures presumed to be necessary for the mercury dibenzyl decomposition.

Previous experiments had indicated that mercury dibenzyl possessed an ultra-violet spectrum having an intense absorption at approximately 260 mμ. This suggested that ultra-violet absorption spectroscopy would provide a satisfactory routine method of analysis for mercury dibenzyl.

(1) The Thermal Decomposition of Mercury Dibenzyl in n-hexane.

A solution of 3.74 mgm. of mercury dibenzyl in 50 ml. of n-hexane (B.D.H. Special for Spectroscopy Grade) was diluted to an extent such that the maximum optical density of the resultant solution was approximately 0.6, when measured in the special silica reaction vessel shown in Fig. 19. against air as standard.

The cell containing the solution was attached to a vacuum system; the solution was then frozen by cooling to -180°C., and the air was pumped out to a residual pressure

of approximately 1 mm., and the constriction was then sealed. The vessel was warmed carefully to room temperature and the initial ultra-violet spectrum of the solution obtained with reference to air. The vessel was then inserted in a boiling water-bath (99-100°C.) for a short time, and after cooling to room temperature a second spectrum was obtained. This indicated a slight loss of starting material. Spectra were obtained after each further period of heating up to a total of 3½ hours, by which time the optical density of the solution was reduced to approximately one-third of its initial value.

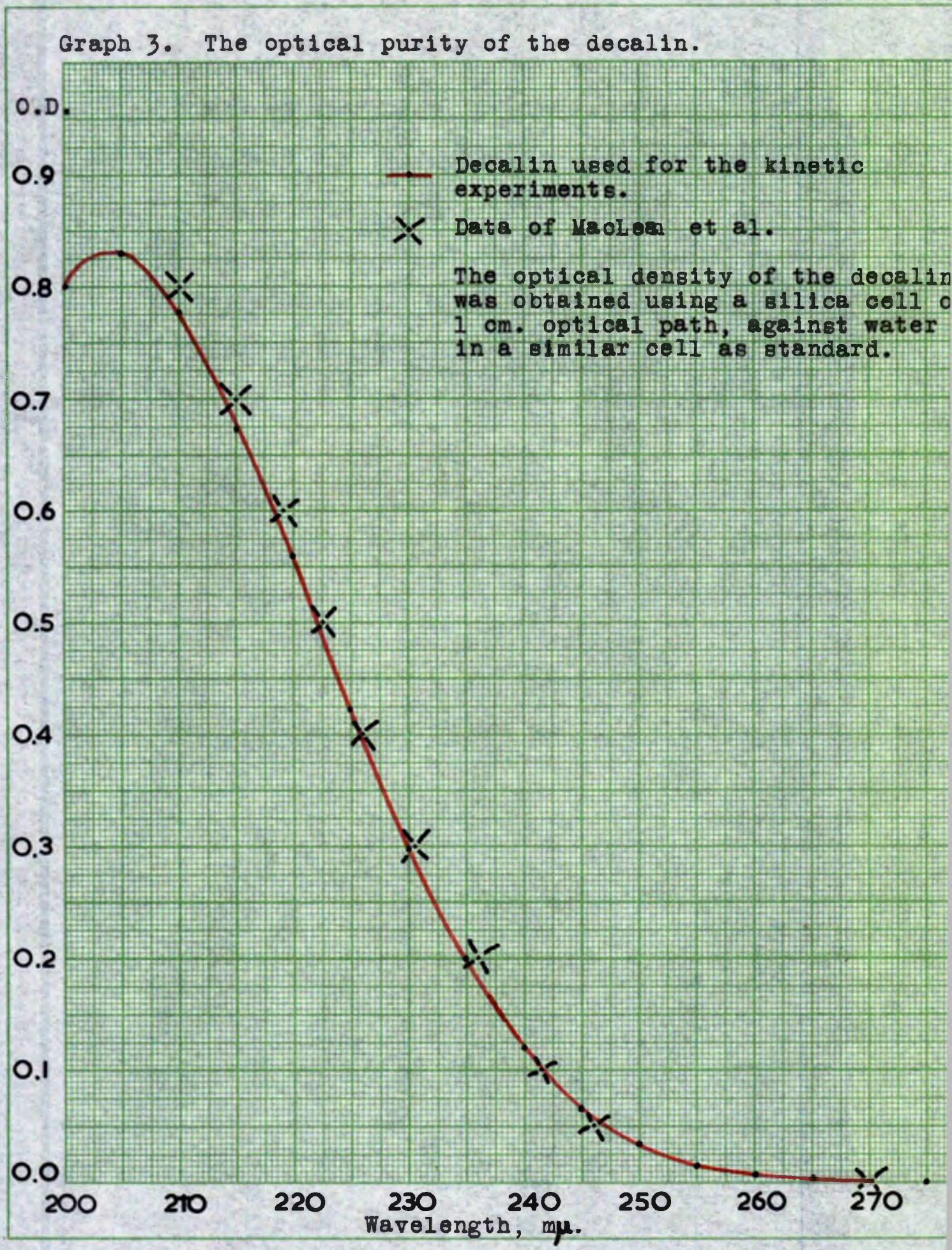
A correction for the absorption of the solvent at the particular wavelengths of interest was obtained by filling the cell with pure solvent and obtaining the spectrum with reference to air.

Plots of $\log_{10}$(optical density(O.D.) of solution - O.D. of solvent, at a particular wavelength) against time were linear.

Two subsequent experiments using a similar technique and portions of the same initial solution failed to produce any appreciable decomposition of the solute, even after 18 hours heating at 100°C.

It was concluded that higher temperatures would be required to produce reasonable rates of decomposition. Since the silica cell in use was judged unsuitable for the high internal pressures which would be created by n-hexane at e.g. 160°C., it was decided that a solvent with a higher boiling point was required.

Graph 3. The optical purity of the decalin.



(2) The Thermal Decomposition of Mercury Dibenzyl in Decalin.

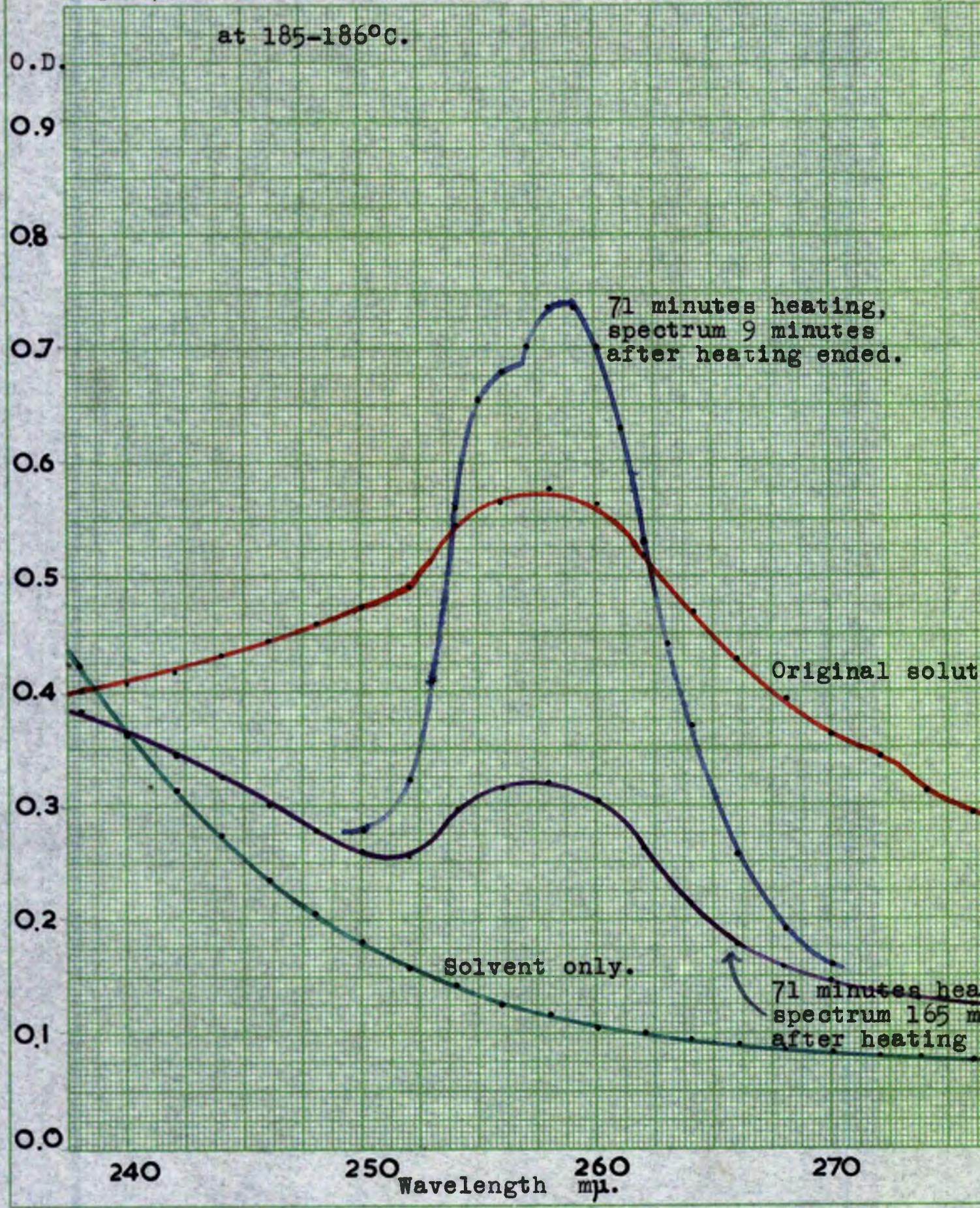
During a literature search for methods of purifying n-hexane for spectroscopic use, the paper by MacLean et al. (37) was consulted. This paper indicated that decahydronaphthalene, decalin, was a readily purified solvent of high b.pt. (b.pt. cis decalin 194.6°C., b.pt. trans decalin 186.7°C.) which was reasonably transparent to ultra-violet radiation.

Laboratory stock decalin was opaque to ultra-violet light in a silica cell of 1 cm. path length.

An attempt to purify this decalin directly by passage down a column of activated silica gel was unsuccessful. Distillation of the decalin under reduced pressure (b.pt. 81.5-82°C. at 32 mm.), followed by passage of the distillate once down a column of activated silica gel produced a spectroscopic quality decalin which was reasonably transparent to ultra-violet radiation, as shown in Graph 3. This stock of spectroscopic decalin was kept under vacuum to prevent peroxide formation.

0.1 ml. of a stock solution of 6.01 mgm. of mercury dibenzyl in 10.0 ml. spectroscopic decalin was diluted to 20.0 ml. with solvent and then placed in a silica reaction vessel which was then attached via a capillary constriction and a tap to a vacuum manifold. The solution was frozen with liquid oxygen, the air pumped out and the tap shut. The solution was melted and re-frozen; the liberated gases were pumped off and the vessel again isolated. A further two degassing cycles were performed, and the cell was then sealed at the constriction.

Graph 4. The decomposition of mercury dibenzyl in decalin, at 185-186°C.



An initial ultra-violet spectrum of the solution was obtained with air as standard. The cell was immersed in the vapour of refluxing aniline (185-186°C.) for 15 minutes, then cooled rapidly to room temperature and a second spectrum obtained.

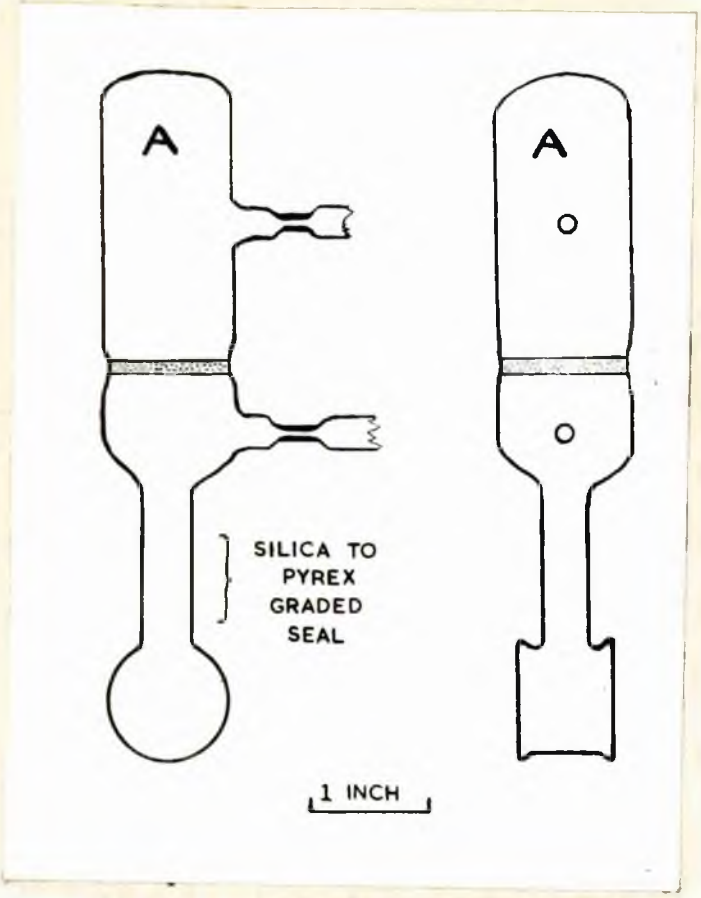
Further spectra were obtained after 35½ minutes and 71 minutes heating. It was found that almost complete decomposition had occurred in under 15 minutes at 186°C. In addition, a broad peak in the region 255-265 mu developed. The intensity of this peak decayed on allowing the cell to stand at room temperature, and reheating the solution caused the peak to reappear. This peak was caused by solution of the metallic mercury produced during the reaction; excess mercury could be observed as shiny globules in the bottom of the cell. A similar spectrum was observed by Phibbs and Darwent (38) for a saturated solution of mercury in decane.

During this experiment it was also observed that the optical density of the reacted solution at wavelengths less than 240 mμ was considerably less than that of the original solvent, measured under similar conditions. This indicated the possibility of some reaction between solvent and solute, or some change in the solvent during the heating. An effect such as this might be expected because of the relatively weak tertiary carbon-hydrogen bonds in the decalin molecule, or because of some reactive impurity in the solvent. Graph 4 shows the observations made during this experiment.

Further experiments were performed at lower temperatures

FIGURE 20.

Fig. 20.



A diagram of the silica reaction cell which was used during some of the experiments with decalin as solvent.

(136-147°C.). The analyses of these experiments required two corrections. Because two similar reaction cells were not available, spectra were recorded with air as standard and then corrected for the solvent absorption by subtraction of the solvent spectrum, determined in the same cell, again with air as standard. A second correction was required because the products of the decomposition absorbed at the wavelengths of interest, although less strongly than the mercury dibenzyl.

The theory of the solvent correction is as follows :- During a determination of the optical density (O.D.) of the solution at a particular wavelength we find $O.D._{soln} = \log(I_o/I)$, where I_o is the intensity of the uninterrupted radiation, and I is the intensity of the radiation after passage through the cell and solution.

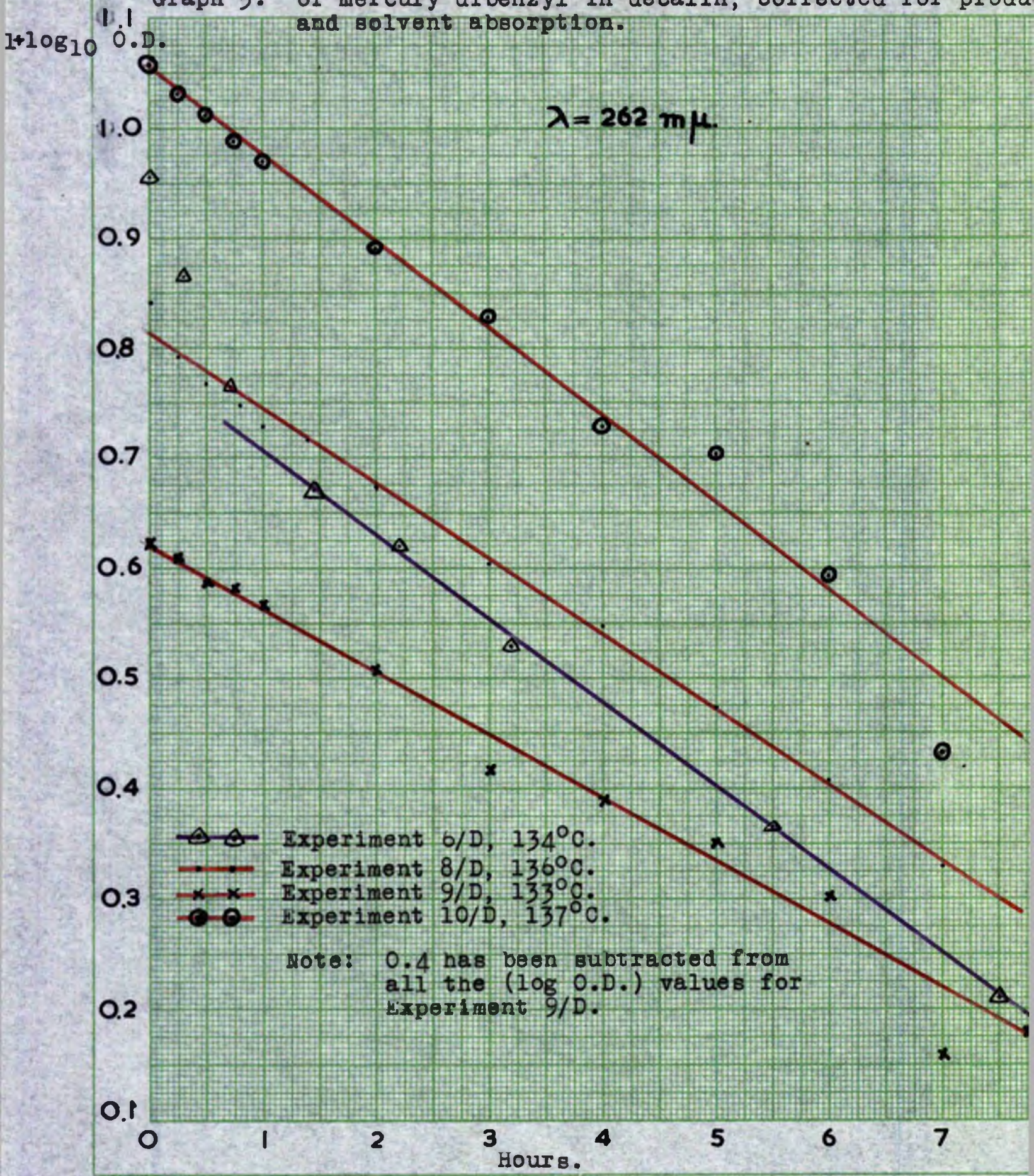
The corresponding equation when measuring the O.D. of the solvent is $O.D._{solv} = \log(I_o/I_1)$, where I_1 is the intensity of the radiation after passage through the cell and solvent.

Ideally, we require the O.D. of the solute only, i.e. $\log(I_1/I)$, which is now seen to be equivalent to $(O.D._{soln} - O.D._{solv})$.

The theory for the correction of the spectra to allow for absorption caused by the products of the reaction is given on page 64 below. The correction for a given wavelength was applied by subtracting from each of the observed O.Ds. at the various times the O.D. of the completely reacted solution.

In spite of these corrections, the data obtained were not

Graph 5. Some of the first-order graphs for the decomposition of mercury dibenzyl in decalin, corrected for produ and solvent absorption.



very consistent e.g. experiments 6/D and 8/D showed reasonable first order decay of mercury dibenzyl, but the reaction at the lower temperature proceeded more rapidly. In addition, the first order plots for some experiments were not linear, e.g. experiment 11/D. Graph 5 shows some of the results obtained.

Several sources of error were found. Although the already noted and very pronounced effect caused by mercury was not reproducible, in certain experiments cloudy solutions developed when the cell was cooled rapidly to room temperature. With slower cooling no such trouble was observed, but there may well have been an effect on the optical absorption of the solution. This effect was also attributed to metallic mercury, and an attempt was made to trap the liberated mercury as it was formed by causing it to amalgamate a clean weighed copper spiral inserted in the neck of the reaction vessel. During experiment 15/D, 1.7 mgm. of mercury was collected on a copper spiral, a retention of only 34%. Mercury globules were visible in the cell unattached to the copper.

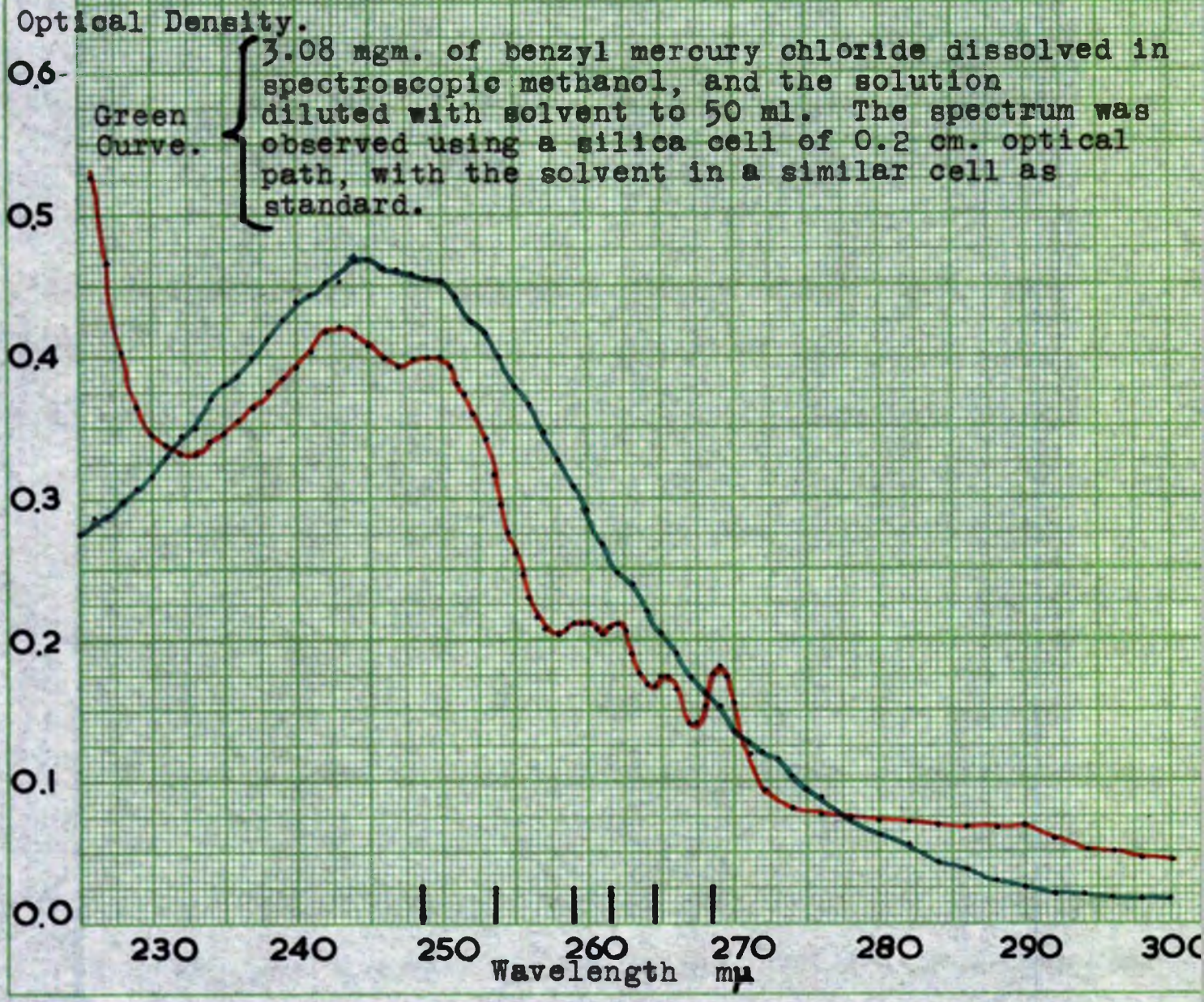
A second method employed to free the solution from mercury was to use a reaction vessel, shown in Fig. 20, divided into two chambers by a No. 4 sintered glass disc.

The decomposition, together with the mercury liberation, was carried out with the solution in chamber A. To measure the optical density the solution was filtered through the disc into the optical cell. After such observations, the solution was repassed through the disc before the whole apparatus was

Graph 6. The products of the thermal decomposition of mercur dibenzyl dissolved in decalin. (Experiment 14/D).

Red Curve: Reaction conditions : 17.9 mgm mercury dibenzyl was dissolved in 15 ml. decalin. The decomposition was carried out at 186°C. for 6¼ hours. 1.02 ml. o the reacted solution was diluted to 10 ml. and the spectrum was obtained using a cell of optical path 1 cm. against solvent in a similar cell as standard

The positions of the major absorption peaks in the spectrum of pure dibenzyl are indicated thus : |



Green Curve. 3.08 mgm. of benzyl mercury chloride dissolved in spectroscopic methanol, and the solution diluted with solvent to 50 ml. The spectrum was observed using a silica cell of 0.2 cm. optical path, with the solvent in a similar cell as standard.

reheated. The disc, although successful in keeping mercury out of the optical cell, permitted only very slow filtration, partly because of the high viscosity of the decalin at room temperature. More rapid filtration was achieved with warm solutions; on cooling, however, colloidal mercury was again produced in the optical cell. The apparatus was not used beyond this preliminary stage.

(2a) The Products of the Decomposition of Mercury Dibenzyl in Decalin Solution.

The products of the decomposition were found to be mercury, which was visible in the bottom of the cell, and a compound or mixture whose ultra-violet spectrum is shown in Graph 6. This most probably represents a mixture of dibenzyl and other components.

A possible second material in the product mixture would have been the strongly absorbing benzyl mercury chloride, which was the intermediate for the synthesis of the mercury dibenzyl. The spectrum of this intermediate is shown in Graph 6. (See also (43)). The purity of the mercury dibenzyl was later re-examined, and the material was recrystallised from iso-octane under vacuum conditions. (See p. 56 et seq.).

Oxygen dissolved in the decalin might account for other products and for the high initial rates of reaction observed in Graph 5, because it was subsequently shown that, at a given temperature, the decomposition of mercury dibenzyl in iso-octane was accelerated by the presence of air. (See p. 74).

On account of the possible solvent-solute reaction, the

high viscosity of the decalin and the difficulty of removing all dissolved gases from so viscous a solvent, a search was made for a more suitable solvent.

(2b) Temperature Control.

At this stage it was realised that much more accurate temperature control would be required than could be obtained in a vapour bath, the temperature of which could vary during the course of an experiment by as much as 10°. because of variations in atmospheric pressure.

An oil filled thermostat was constructed with a main electrical heater which could be adjusted to maintain a steady bath temperature some 2-5C°. below the required value. A subsidiary heater was operated, via an electronic relay device, by a toluene-type mercury regulator filled with degassed di-(n-butyl) phthalate. With this subsidiary heater in operation, the temperature was never more than ± 0.15C°. from the mean value.

(3) The Thermal Decomposition of Mercury Dibenzyl in iso-octane.

As described above, the decompositions of mercury dibenzyl in n-hexane and decalin were not very successful in leading to data which were capable of simple interpretation.

On the basis of the work already described it seemed that the use of an alternative solvent might ease some of the difficulties. The desired solvent would possess the following properties :-

(a) a high transparency to radiation in the wavelength region 200-300 mμ.

(b) a resistance to attack by free radicals arising during the decomposition of mercury dibenzyl.

(c) a high b.pt., thus enabling glass vessels of simple design to be used as reaction vessels at temperatures up to 180°C., without undue risk of fracture by the pressures created.

(d) good solvent properties for mercury dibenzyl.

(e) a low viscosity at room temperature to enable degassing to be readily achieved.

(f) high stability to oxidation when kept for prolonged periods.

In addition the material had to be readily available and easily purified.

The only type of solvent meeting all these requirements would be a paraffinic hydrocarbon. The b.pt. of the n-hexane already used was too low (b.pt. 68.7 °C.) to permit safe usage in the silica reaction cells at temperatures above 100°C.

Iso-octane, 2,2,4-trimethyl pentane, b.pt. 99.2°C., was commercially available in a spectroscopically pure grade (Messrs B.D.H. Ltd.). In spite of its higher boiling point, it was considered that it would be unsafe to use iso-octane in the silica reaction cells at temperatures above 120°C., and a new experimental technique was developed, as described below.

A sample of this solvent was investigated, and found to be satisfactory. Experiments 1/I to 14/I were performed in this B.D.H. Spectroscopic Grade iso-octane, used without further purification.

In all the subsequent experiments Esso Reference Grade

Fuel iso-octane which had been purified by chromatography according to the method of MacLean, Jencks and Acree (37) was used. The essential details of the purification procedure were as follows. The Reference Grade iso-octane was passed down a glass tube (size 1.7 cm. diameter, 38 cm. long) packed lightly with activated silica gel (100-200 mesh).
The activation of the gel was achieved by soaking the gel in distilled water for several hours, removing the water and displaced solvent by filtration, and drying the gel at a temperature below 300°C. in a wide-necked flask over a Bunsen flame.

Samples of approximately 40 ml. of solvent from the columns were collected and their optical densities determined at various wavelengths, using a silica cell of 1 cm. path length, against distilled water in a similar cell as standard.

The 2½ litres of solvent obtained from the first passage down the silica columns was repassed down fresh columns. Samples were checked for optical purity as previously, before batches were accepted as final solvent I. The optical quality of the 2 litres of final solvent I compared favourably with that quoted for the iso-octane prepared by MacLean et alia (37). Typical data for the solvent purification are quoted in Table 4 and on Graph 7.

It will be noticed for the final solvent I that the components in the Reference Grade Fuel which caused the absorption at wavelengths greater than 230 mμ have been

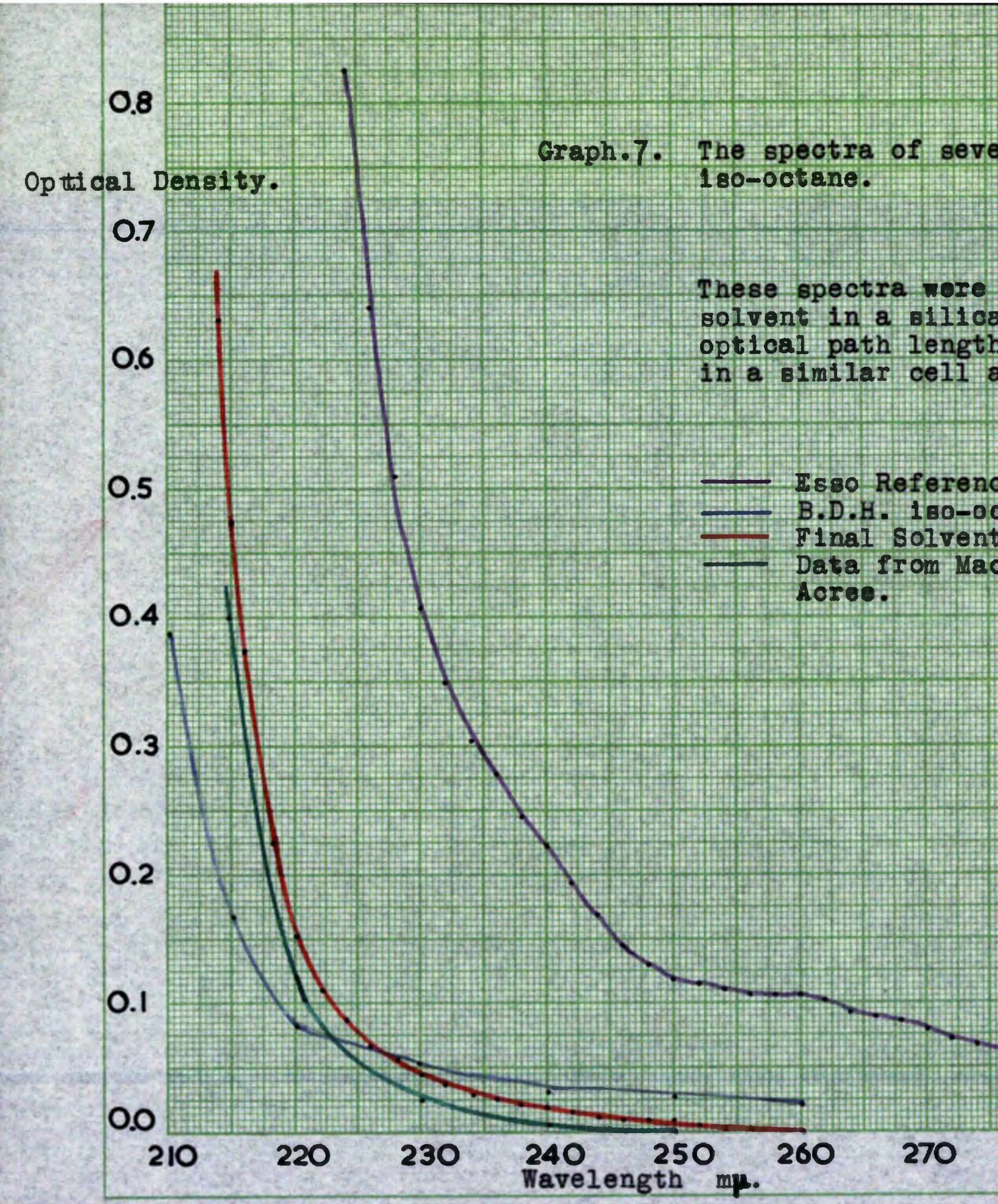

Graph.7. The spectra of seve
iso-octane.
These spectra were
solvent in a silica
optical path length
in a similar cell a
Esso Referenc
B.D.H. iso-oc
Final Solvent
Data from Mac
Acree.
Optical Density.
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
210
220
230
240
250
260
270
Wavelength mμ.

Table 4.

Optical densities of various iso-octane samples, taken against distilled water as standard, in silica cells of 1 cm. optical path length.

Wavelength mμ. / Sample	210	220	230	240	250	260	Disposal
B.D.H. iso-octane	0.440	0.158	0.080	0.056	0.051	0.046	Experiments 1-14/I.
Esso Reference Grade Fuel		1.22	0.410	0.222	0.120	0.107	Feed to columns.
First Column							
First sample	0.850	0.425	0.365	0.222	0.156	0.156	Reject.
Second sample	0.700	0.114	0.054	0.026	0.012	0.015	Accept.
Ninth sample	1.75	0.140	0.052	0.022	0.010	0.010	Accept.
Tenth sample	2.	0.430	0.086	0.022	0.011	0.009	Reject.
Seventh Column							
First sample	---	0.085	0.026	0.008	0.000	0.000	Accept.
Ninth sample	---	0.455	0.061	0.007	0.000	0.000	Accept. ϕ
2½ l. of solvent	1.65	0.202	0.067	0.040	0.030	0.026	Feed for second passage.
Final Solvent I	1.52	0.154	0.046	0.020	0.014	0.012	Experiments 15-37/I
Final Solvent II	---	0.203	0.054	0.019	0.009	0.014	Experiments 38/I onwards.
MacLean, Jencks and Acree	1.4	0.120	0.027	0.010	0.000	0.000	---

ϕ The eighth column was used after this sample had been collected.

almost completely removed, whilst the lower capacity of the silica for the components causing the absorption at wavelengths less than 220 mu. makes it more difficult for these impurities to be as readily abstracted.

The purity of solvents used for kinetic experiments is usually a matter of considerable importance (39). Reference Grade Fuel is usually quoted as 98-99.9% pure, and as the impurities were likely to be other hydrocarbons (40), such traces of these were not considered likely to cause complications, unless they were of an unsaturated character or contained weakly bonded hydrogen atoms. The final solvent I was considered to be of much greater purity, and hence no complications were to be expected from impurities during the use of this purified solvent for kinetic work, even when very dilute solutions of reactant were employed.

It was observed that on evaporation of large volumes of the B.D.H. Spectroscopic Grade iso-octane a small quantity of an involatile material remained. To check this, 1 ml. samples of the B.D.H. solvent and the final solvent I were evaporated in pre-weighed vessels. The B.D.H. solvent gave a visible trace of residue which weighed 0.00006 gm., whilst the final solvent I gave no detectable residue.

All solvent I residues from the kinetic and other experiments were retained, and passed once down a fresh column of activated silica gel. This produced a supply of final solvent, II, which was used for experiments 38/I onwards.

(3a) The Solubility of Mercury Dibenzyl in iso-octane.

It was observed during experiment 9-10/I that incomplete degassing of the solution in one of the reaction vessels led to an abnormally rapid rate of reaction. This observation could, of course, have been an experimental error in the determination of the concentration of the residual mercury dibenzyl in the solution, but experimental proof that oxygen did in fact affect the rate of the decomposition was needed in order to justify the solution degassing procedure adopted during the preparation for experiments. Experiments 13/I and 14/I were therefore carried out in un-degassed solvent, and very abnormal results were obtained, as described below.

As a result of this work it was considered desirable to re-examine the purity of the stock mercury dibenzyl. This had been twice recrystallised from hot ethyl acetate, as described on page 30, during which it might have been possible for a reaction to have occurred between the solute and atmospheric oxygen, thus forming an impure product.

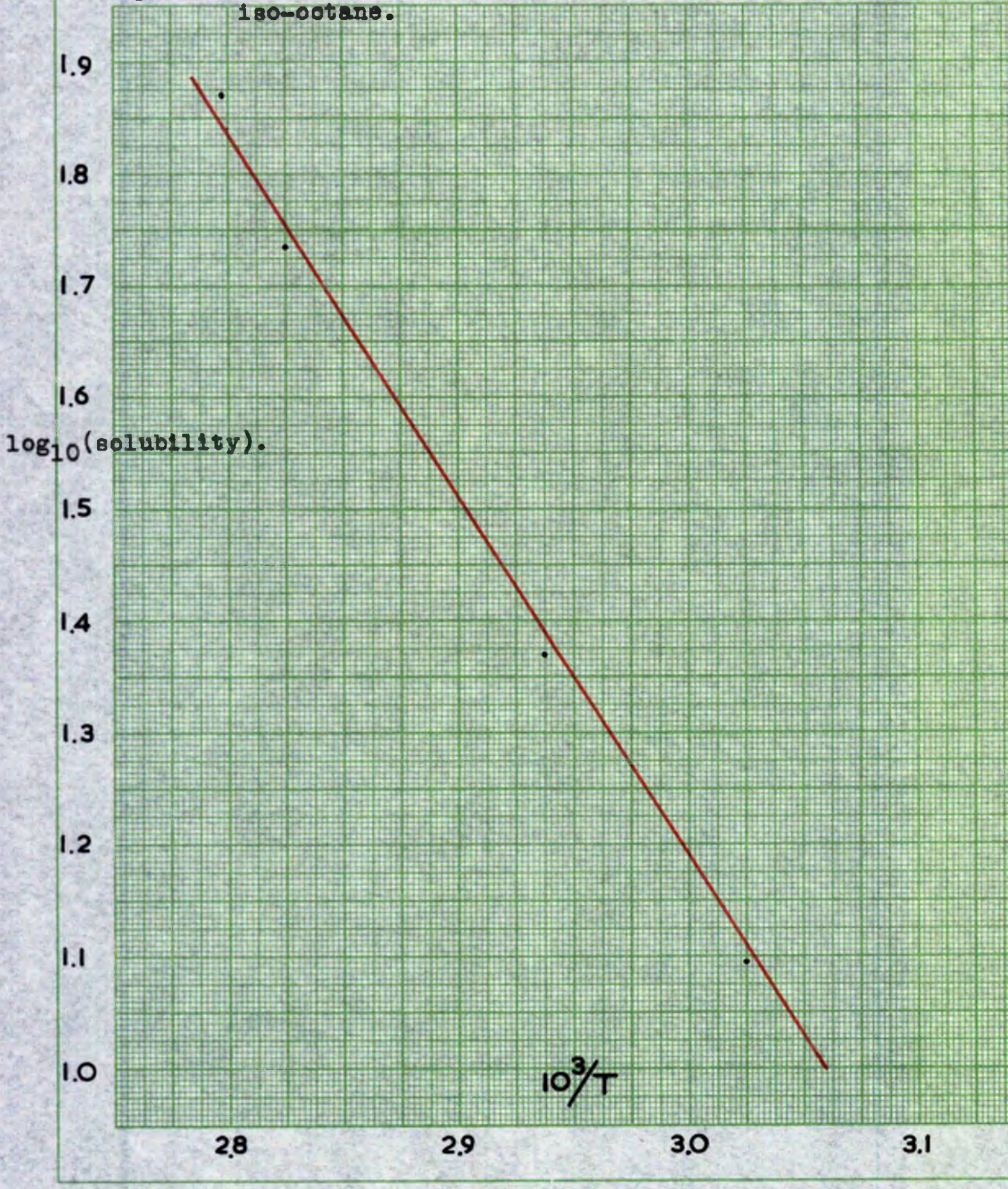
It was decided that the stock of mercury dibenzyl, as used for experiments 1/I to 14/I, should be recrystallised, in vacuo, from the degassed final solvent I. As a preliminary to this, the solubility of the mercury dibenzyl in iso-octane at various temperatures was required.

(3b) The Determination of the Solubility of Mercury Dibenzyl in iso-octane.

Small vessels of the type used for the kinetic experiments and prepared in the same manner, as described on page 61, were weighed clean and dry. Various quantities of the stock mercury dibenzyl were added and the vessels reweighed. 1.0 ml. of the B.D.H. iso-octane was added to each vessel via a fine funnel, from a 1 ml. calibrated pipette. The solutions were then degassed by the procedure described on page 62, and the vessels were sealed.

Initial attempts to determine the temperature at which the solutions became just saturated by cooling the vessels slowly from higher temperatures proved to be unreliable because the solutions showed a tendency to supercool. The technique finally adopted was as follows. A vessel, held in a wire cradle, was placed in a clean beaker containing 350 ml. of distilled water, a thermometer and a stirrer. The temperature of the water was raised slowly, and the vessel agitated. The water temperature when all the crystals had dissolved gave an approximate solution temperature. The larger crystals, however, took a considerable time to dissolve, and errors could have occurred. The vessel was then removed from the hot bath and cooled rapidly in liquid oxygen. This produced a very fine precipitate within the solid solvent. The water in the beaker was cooled to a temperature somewhat below the approximate solution temperature, and the vessel replaced. The solvent

Graph 8. The solubility data for mercury dibenzyl dissolved in iso-octane.



melted and the bulk of the very fine precipitate dissolved, leaving numerous small crystals which were readily visible in strong oblique illumination. Vigorous agitation of the vessel ensured temperature equilibrium. The temperature of the bath was then slowly raised, and the temperature at the disappearance of the last of the small crystals was recorded as the solution temperature. The results are recorded in Table 5. The efficiency of the technique may be judged by the linearity of the plot of $\log_{10}$(solubility) against ($1/T^{\circ}A$), as shown in Graph 8. From this data, which is not of great accuracy, the heat of solution of mercury dibenzyl in iso-octane was calculated to be 14.8 kcal./mole.

Table 5.
The solubility of mercury dibenzyl in iso-octane.

mgm. mercury dibenzyl in 1.0 ml. solvent.	Temperature at which complete solution was attained. °C.
12.5	57.5
23.5	67.5
54.3	81.0
74.0	84.5

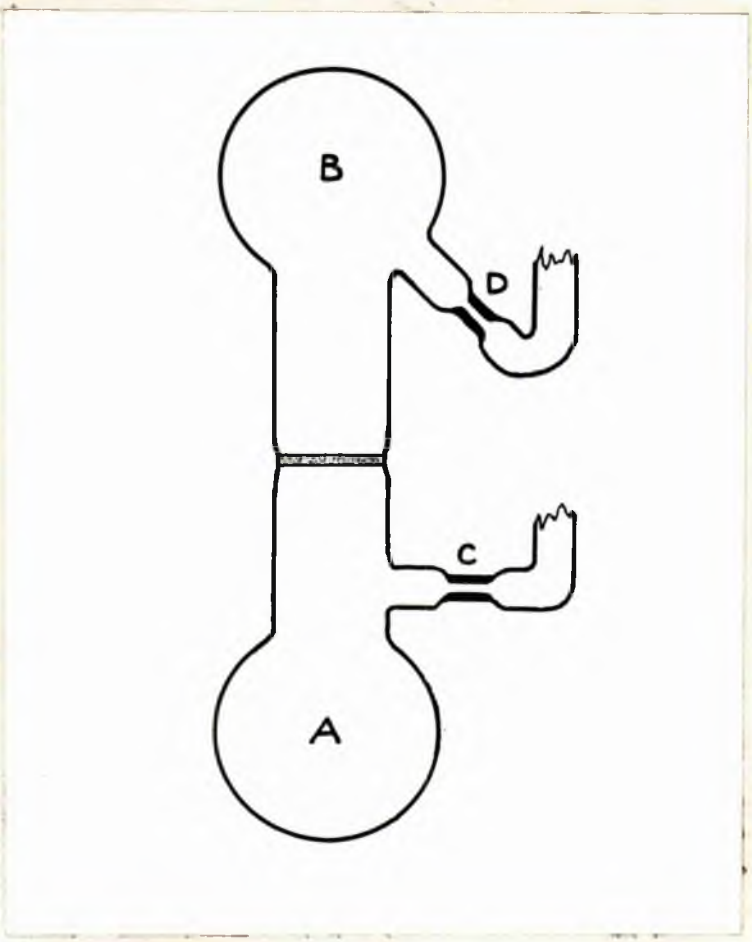
(3c) Recrystallisation of the stock Mercury Dibenzyl from iso-octane in Vacuo.

From experiments 1/I to 14/I it was estimated that 2 gm. of purified mercury dibenzyl would be required for analyses and further kinetic experiments.

Because of the instability of mercury dibenzyl it would be unwise to heat a solution of the material to a temperature exceeding 80°C., even in the absence of air, for a prolonged period.

FIGURE 21.

Fig. 21.



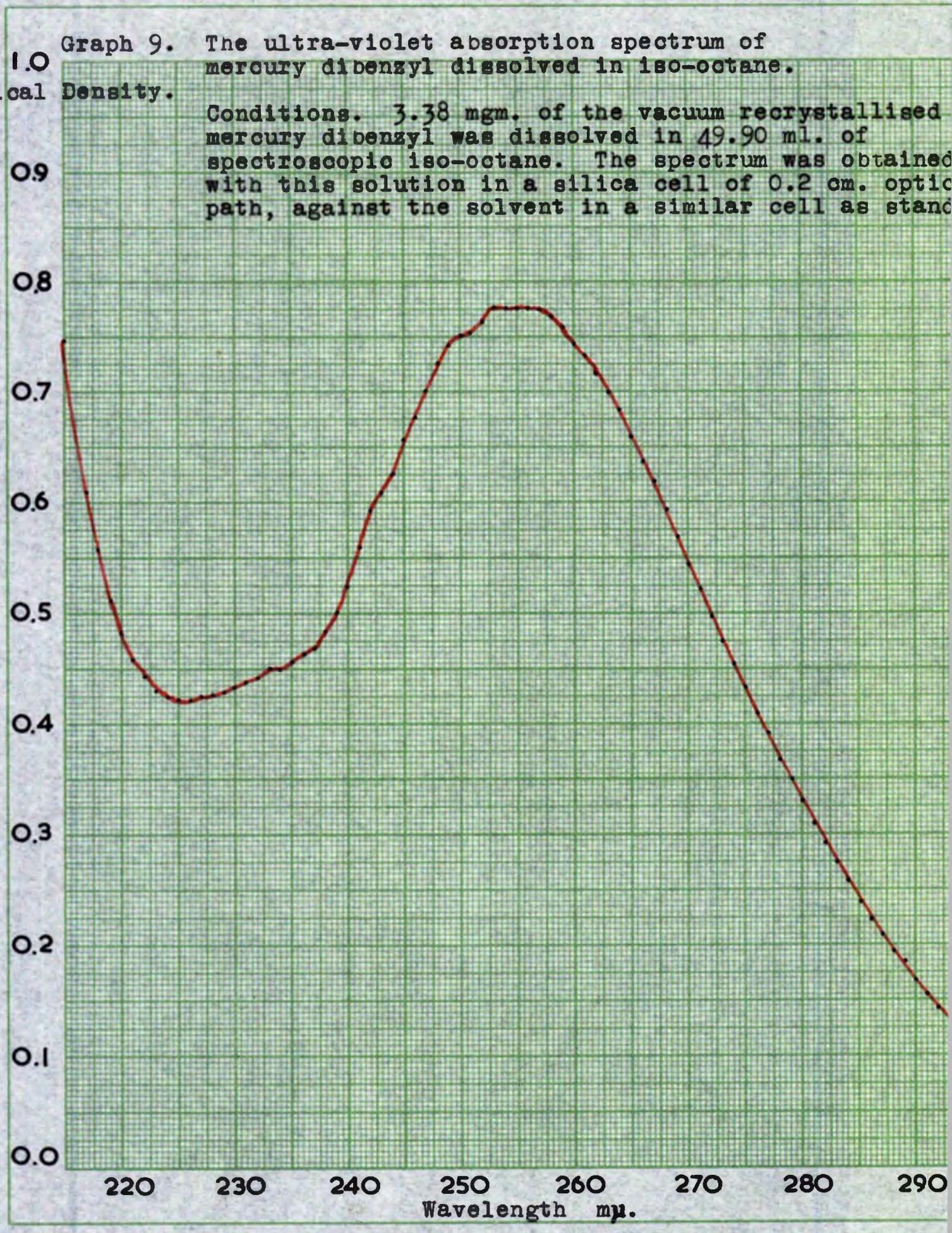
A diagram of the vessel used for the vacuum recrystallisations.

From the solubility data, to obtain a solution which contained 2 gm. of material at 80°C. would require approximately 40 ml. of solvent. The vessel used for the vacuum recrystallisation is shown in Fig. 21. The method of use was to introduce 1.99 gm. of the stock mercury dibenzyl together with approximately 40 ml. of the final solvent I into the 100 ml. bulb A. The apparatus was next attached, via the two constrictions C and D and two taps to a high vacuum line, with the axis AB vertical, B uppermost. The solvent and solid in A were frozen with liquid oxygen, and the solvent was degassed three times, as described on page 62; the constrictions were then sealed, the apparatus was removed and completely immersed, with B uppermost, in water which was slowly heated to 93°C., at which temperature complete solution of the solid occurred.

The apparatus was then removed from the water, rapidly inverted - the lower bulb B was cooled slightly with a cloth soaked with cold water so as to drive the solution through the No. 4 sintered disc - and then re-inserted in the hot water bath. The bath was thermally insulated, and the whole system was allowed to cool during 16 hours to room temperature. Long shining white needles were produced. The apparatus was removed from the water bath and again inverted, and bulb A immersed in liquid oxygen. This drove the solution from B into A, where it froze, and excess solvent was removed from the crystals left in the upper bulb B. Constriction C was opened, and dust-free air admitted to bulb B. Constriction D was then opened and the crystals were washed with 2 ml. of the

Graph 9. The ultra-violet absorption spectrum of mercury dibenzyl dissolved in iso-octane.

Conditions. 3.38 mgm. of the vacuum recrystallised mercury dibenzyl was dissolved in 49.90 ml. of spectroscopic iso-octane. The spectrum was obtained with this solution in a silica cell of 0.2 cm. optic path, against the solvent in a similar cell as stand



final solvent which was then sucked off through the disc. The crystals were then removed to their final tared storage vessel, and then dried under vacuum. The yield of purified crystals was 1.82 gm. (91%). The m.pt. of these crystals in air was 110.2-111.6°C. (corrected). A very fine hair-like sublimate formed on the cover glass of the micro-stage of the melting point apparatus at temperatures above 100°C. This sublimate was removed, and it melted at 103-105.8°C. (corrected). Thus, it was concluded that the mercury dibenzyl decomposed when heated to high temperatures in air. After it had been sealed in an evacuated capillary tube, the recrystallised mercury dibenzyl showed no appreciable change in m.pt.

An analysis of this recrystallised mercury dibenzyl by the gravimetric method was reported above.

(3d) <u>The Spectral Absorption of the Purified Mercury Dibenzyl</u>.

Standard solutions of mercury dibenzyl were prepared from samples of the solid weighed on a semi-micro balance, and for standard solutions No. 5 and onwards the total weight of the stand, vessel and contents was so adjusted that only differences between the rider weights of the balance were required to weigh samples. Samples were transferred to volumetric flasks calibrated at room temperature, dissolved in solvent and the volumes made up to the mark.

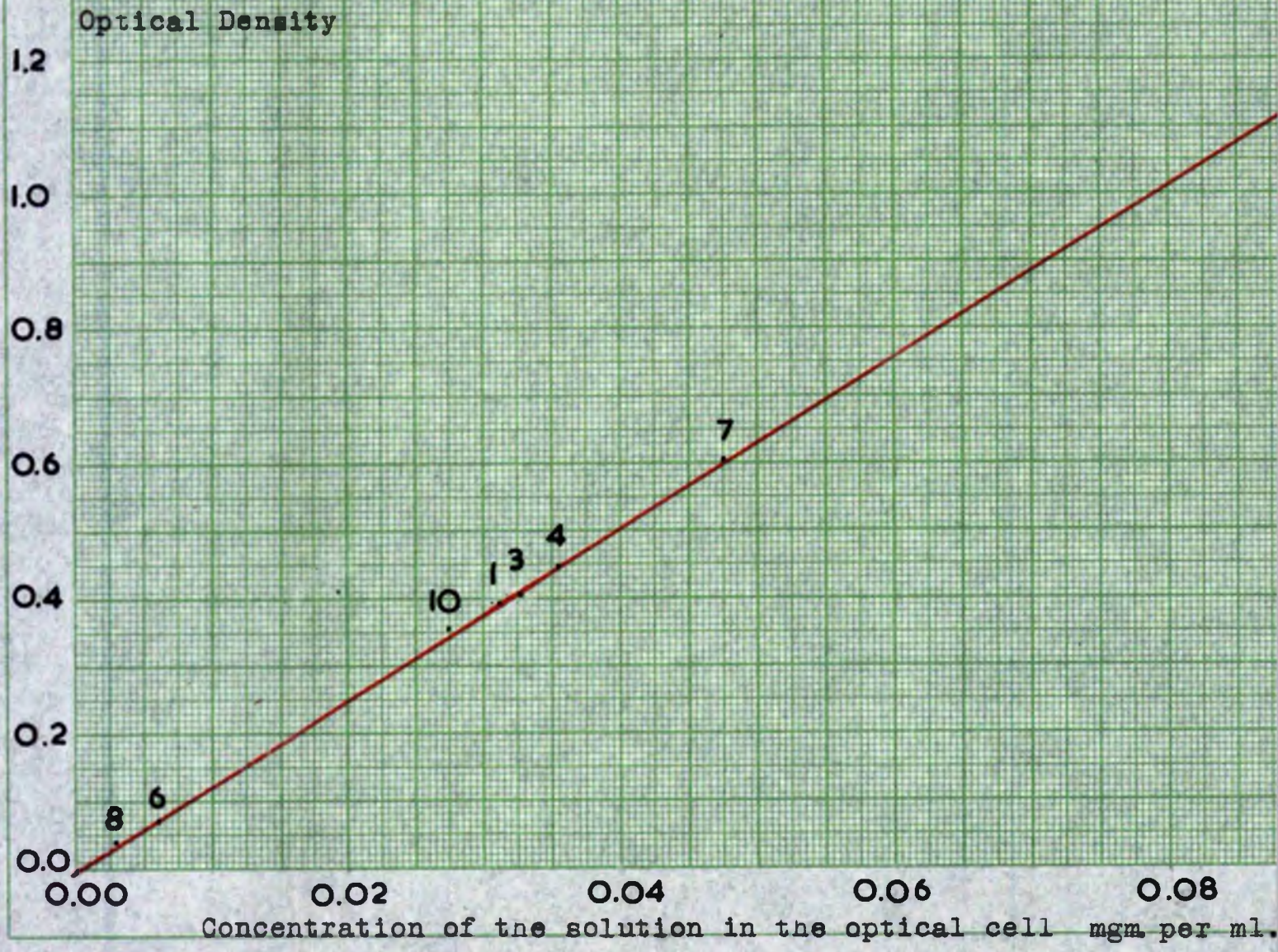
The absorption spectrum of the purified mercury dibenzyl in the final solvent I is shown in Graph 9.

The stability of the solutions, kept in the dark at room

Graph 10. The optical densities of the standard solutions of mercury dibenzyl in iso-octane, at 255 mμ.

These observations were recorded with the solutions in a cell of 2 mm. path length, against solvent in a similar cell as standard.

The figure above the point refers to the standard solution (See Appendix 4).



temperature, is indicated below; the change in the optical density of the solution is considered mainly due to experimental error, with perhaps some slight solvent evaporation.

Scale mu	225	242	250	272	290
30 Sept. O.D.	0.327	0.427	0.563	0.382	0.128
25 Oct. O.D.	0.337	0.445	0.576	0.385	0.131
The O.D. are the mean values of five readings at each wavelength on the date indicated.					

The consistency of the spectral data obtained from the standard solutions used during the kinetic investigations is illustrated by Graph 10.

(3e) <u>The Description of an Experiment</u>.

Short lengths of pyrex glass tube (10 mm. internal diameter) which had been carefully cleaned by prolonged treatment in boiling concentrated nitric acid, followed by two prolonged washings in boiling distilled water, were formed into reaction vessels of 2 ml. capacity, closed at one end, with a thick-walled capillary constriction at the other joined to a B 10 ground glass cone. After construction the vessels were evacuated and heated for a short period at just below the softening temperature to remove any volatile material. The vessels were then removed from the vacuum line and were roasted at a glowing temperature for approximately one minute to clean the internal surface of each tube thoroughly.

Groups of 12 vessels were then filled, via a fine funnel, with aliquots, usually 0.5 ml., of a standard iso-octane solution of mercury dibenzyl.

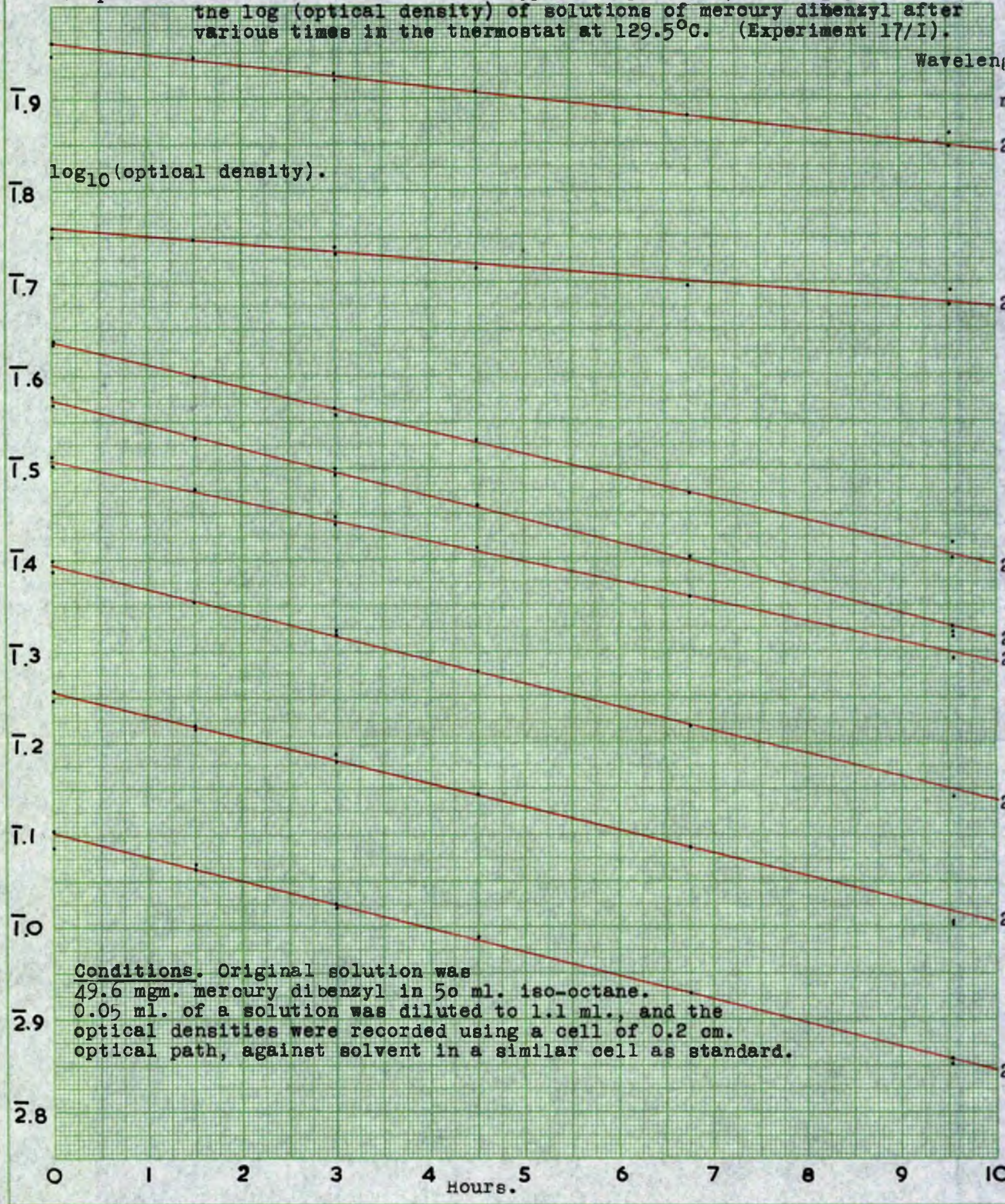
The filled vessels were then attached to B 10 sockets, each of which was isolated from a vacuum line by a tap. With the taps shut, liquid oxygen cooling was applied to each of the vessels. When the solutions had frozen completely, the taps were opened and the vessels evacuated to less than 10^{-3} mm.. The taps were shut, and each vessel was allowed to warm up to room temperature. During this first degassing operation a considerable quantity of gas was liberated from the melting solid. The solutions were re-frozen with liquid oxygen cooling; when frozen the taps were opened and the liberated gases were pumped out, and then each vessel was re-isolated. With the most dilute solution, four such degassing cycles were found to be necessary in order to obtain consistent kinetic results. With the more concentrated solutions three degassing cycles were sufficient.

After the final degassing cycle a Tesla Coil discharge detected a small quantity of gas over the frozen solutions. Slightly turning a tap increased the intensity of the discharge, thus suggesting that this gas was liberated from the tap grease. With the solutions frozen and full pumping applied, each vessel was sealed at its constriction and removed.

The freezing procedure caused the precipitation of most of the mercury dibenzyl as a film on the walls of the vessels. These precipitates were redissolved by prolonged agitation of the vessels, before the decompositions were attempted.

The vessels were immersed in a thermostat, at a known time,

Graph 11. Some of the results for a typical experiment, showing plots of the log (optical density) of solutions of mercury dibenzyl after various times in the thermostat at 129.5°C. (Experiment 17/I).



Conditions. Original solution was 49.6 mgm. mercury dibenzyl in 50 ml. iso-octane. 0.05 ml. of a solution was diluted to 1.1 ml., and the optical densities were recorded using a cell of 0.2 cm. optical path, against solvent in a similar cell as standard.

in groups of ten. Pairs of vessels were removed at known times and cooled rapidly in cold water. In later experiments, a pair of vessels was left in the thermostat until decomposition was complete. One or two vessels were unheated, and served to check that no appreciable increase in concentration of the solutions had occurred during the degassing procedures.

Analyses were carried out by opening the vessels, removing known volumes of the solutions with self-setting micro-pipettes and diluting them to 1.10 ml. with the pure solvent in a specially constructed standard flask, and observing the optical densities of the resultant solutions, against pure solvent as standard, at various wavelengths in the region of the maximum absorption of mercury dibenzyl using silica cells of 2 mm. optical path.

Plots of $\log_{10}$(O.D. of the solution at a particular wavelength) against time were almost linear, thus showing essentially first order decomposition of the mercury dibenzyl. These plots for any one experiment, although linear, did not all possess equal slopes. This was unexpected for a first order decomposition if the mercury dibenzyl was the only contributor to the absorption at these wavelengths. In an attempt to discover the reason for these discrepancies, the range of wavelengths over which measurements were made was extended. The results for a typical experiment are shown in Graph 11.

Initially, it had been assumed that since the extinction coefficient of mercury dibenzyl was about 50 times larger than

that of the product dibenzyl, the contribution of the latter to the total optical density could be neglected. The high reproducibility of the data, illustrated in Appendix 1, showed that this simplification was not suitable and a method of correction for the dibenzyl absorption was evolved and is described in the next section.

(3f) The Method of Allowing for the Dibenzyl Absorption.

The observed optical densities of the solutions were corrected for product absorption by the following method :-

For a material decomposing according to the first order law we have :

$$c_t = c_0 . e^{-kt}$$

where c_t = concentration of material at time t seconds.
c_0 = concentration of material at time 0 seconds.
e = exponential base of logarithms.
k = specific rate constant in seconds^{-1}.
t = time in seconds from the start of the reaction.

If, in addition, the solutions of the pure reactant obey Beer's Law, we have :

$$\text{Optical Density (O.D.) at } \lambda_1 = \log_{10}(I_0/I) = \epsilon_{\lambda_1} . c . d$$

where I_0 = intensity of the radiation transmitted through the solvent at wavelength λ_1.
I = intensity of the radiation transmitted through the solution at wavelength λ_1.
ϵ_{λ_1} = molar extinction coefficient of the material at wavelength λ_1.
c = concentration of the solution in moles/litre.
d = optical path length of the solution in cm.

Thus, for measurements at a particular wavelength λ_1, we have :

$$\text{O.D. at time } t = (\text{O.D. at time } 0).e^{-kt},$$

if the products of the reaction do not absorb at this wavelength.

Therefore, $\log_{10}$(O.D. at time t) when plotted against t should give a linear graph with slope $(-k/2{\cdot}303)$.

For the simple decomposition $A \rightarrow B + C$, the concentration of the product B at time t seconds, c'_t, is given by :

$$c'_t = c_0.(1 - e^{-kt}) \quad .$$

If the solutions of the product B also obey Beer's Law, we have :

$$\text{O.D. at time t caused by product B alone} = \epsilon'_{\lambda_1}.c'_t.d$$
$$= \epsilon'_{\lambda_1}.d.c_0.(1-e^{-kt})$$

where ϵ'_{λ_1} the molar extinction coefficient for the product B at wavelength λ_1.

If mixtures of reactant and product B obey Beer's Law, we have for the reaction mixture at time t, assuming that product C does not contribute to the absorption at λ_1 :

$$\text{O.D. mixture} = \text{O.D. reactant} + \text{O.D. product B.}$$
$$= \epsilon_{\lambda_1}.d.c_0.e^{-kt} + \epsilon'_{\lambda_1}.d.c_0.(1 - e^{-kt}) \quad ,$$

or $(\text{O.D. mixture} - \epsilon'_{\lambda_1}.d.c_0) = d.c_0.(\epsilon_{\lambda_1} - \epsilon'_{\lambda_1}).e^{-kt}$,

or $\log_e(\text{O.D. mixture} - \epsilon'_{\lambda_1}.d.c_0) = \log_e\left[d.c_0.(\epsilon_{\lambda_1} - \epsilon'_{\lambda_1})\right] - kt$.

Thus $\log_{10}(\text{O.D. mixture} - \epsilon'_{\lambda_1}.d.c_0)$ plotted against t should give a linear graph with slope $(-k/2{\cdot}303)$. The term $\epsilon'_{\lambda_1}.d.c_0$ was readily found as it was the optical density of the solutions in which the decomposition was complete.

If the second product, C, also absorbs at wavelength λ_1, another term $\epsilon''_{\lambda_1}.d.c_o.(1 - e^{-kt})$ is introduced but a new expression $-(\epsilon'_{\lambda_1}.d.c_o+\epsilon''_{\lambda_1}.d.c_o)$ is then obtained in the final equation. This expression is again the O.D. of the solutions in which 100% decomposition occurs, and thus the method of analysis is still satisfactory.

(3g) The Data for an Experiment in iso-octane.

The data collected during the course of an experiment are given in Table 6 and Graph 12. The data at all wavelengths are corrected for product absorption, although the corrections needed at wavelengths 272 mμ., 280 mμ., 285 mμ. and 290 mμ. were so small that they could have been neglected.

In general, the rate constants calculated from corrected data agreed well with those calculated from data where no correction was needed, thus indicating the validity of the theory presented in (3f). (Compare Graphs 11 and 12).

(3h) The Data for all the Experiments with Mercury Dibenzyl in iso-octane.

The first order velocity constants, determined from the graphs of $\log_{10}$(O.D. of solutions at wavelengths 272 mμ or 290mμ) against time , for the decomposition of mercury dibenzyl in iso-octane in the absence of air are given in Table 7. The decompositions, some of which were followed to 90% reaction, followed the first order law accurately.

Graph 12. Data for Experiment 17/I, corrected for product absorption.

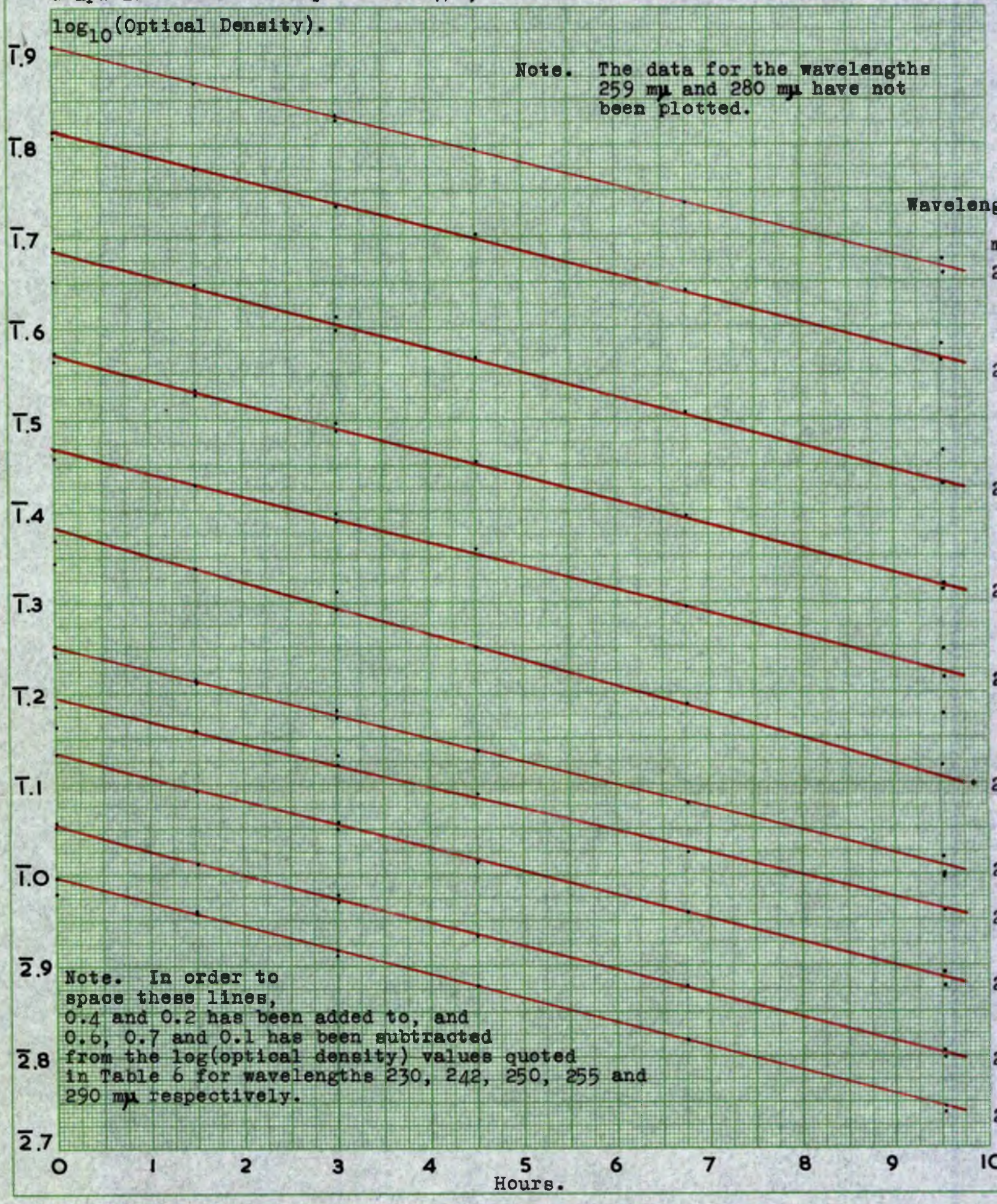


Table 6. Data for Experiment 17/I, corrected for product absorption.

Temperature of thermostat 129.5°C.

For each analysis, 0.05 ml. of the reacted solution was removed from a reaction vessel with a content pipette and diluted to 1.02 ml. with spectroscopic iso-octane in a calibrated standard flask. (See ϕ at foot of table).

The optical densities of the diluted solutions were determined at the various wavelengths against spectroscopic iso-octane as standard, using silica cells of 0.2 cm. optical path length.

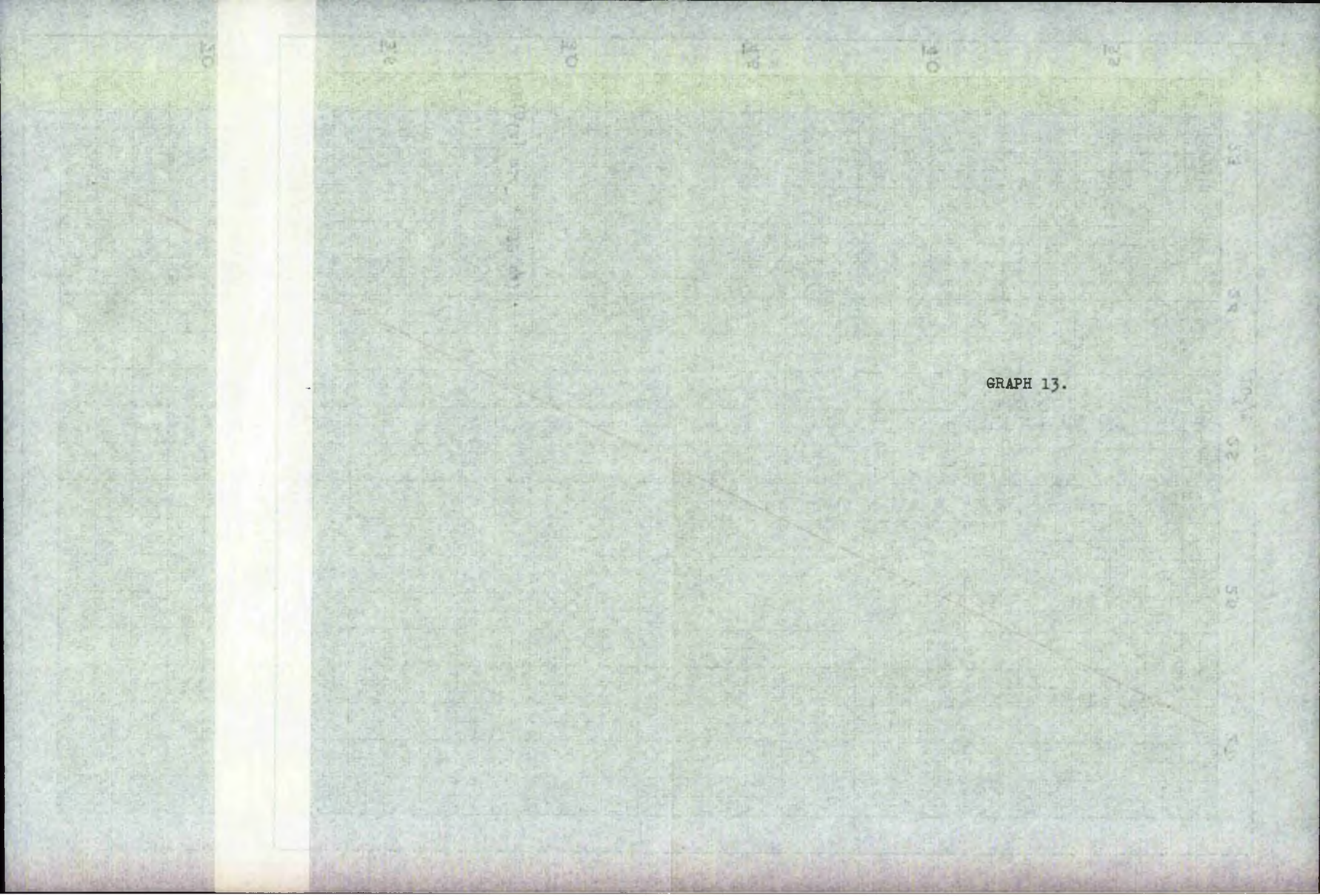
Five readings of the optical density were recorded at each wavelength, and the average value obtained. This average value was corrected for product absorption. The $\log_{10}$ of the corrected optical densities thus obtained are recorded in the table.

Note. 2.000 has been added to all the log values recorded below.

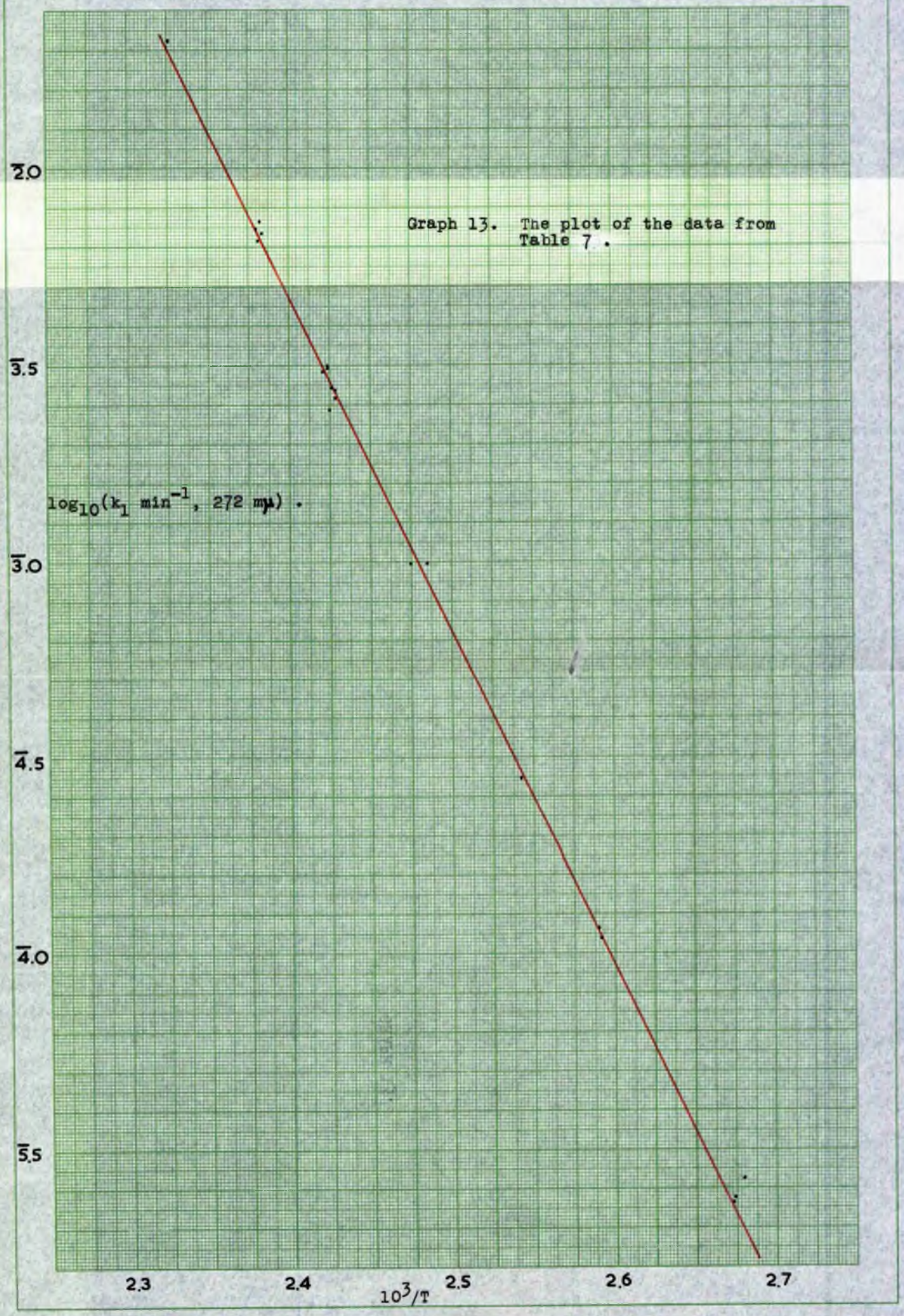
Time	λ 210	215	220	225	230	242	250	255	259	272	280	285	290
0.S. ϕ	1.687	1.367	1.185	1.468	1.508	1.614	1.732	1.756	1.742	1.573	1.395	1.253	1.097
0.S.	1.650	1.342	1.164	1.458	1.500	1.611	1.732	1.752	1.738	1.565	1.382	1.241	1.079
1' 31"	1.646	1.339	1.161	1.428	1.468	1.575	1.692	1.714	1.698	1.529	1.350	1.215	1.061
1' 31"	-	-	-	-	-	-	-	-	-	1.530	-	1.212	1.057
3' 1"	1.598	1.295	1.121	1.387	1.430	1.533	1.651	1.670	1.660	1.490	1.314	1.173	1.013
3' 1"	1.614	1.312	1.134	1.396	1.435	1.539	1.657	1.676	1.663	1.496	1.318	1.182	1.017
4' 30"	1.568	1.250	1.090	1.358	1.395	1.502	1.615	1.633	1.622	1.455	1.274	1.137	0.978
6' 46"	1.509	1.188	1.025	1.297	1.337	1.439	1.558	1.578	1.564	1.396	1.212	1.079	0.919
9' 32"	1.430	1.121	0.960	1.218	1.258	1.364	1.479	1.500	1.486	1.316	1.134	0.996	0.839
9' 32"	1.467	1.176	1.017	1.248	1.274	1.382	1.491	1.505	1.489	1.320	1.134	1.000	0.845

O.S. indicates that the solution was not heated.

ϕ indicates that the solution was obtained by diluting 0.05 ml. of the original standard solution of 49.6 mgm. of mercury dibenzyl in 50 ml. iso-octane which, unlike the other solutions, had not been sealed in a reaction vessel.



GRAPH 13.

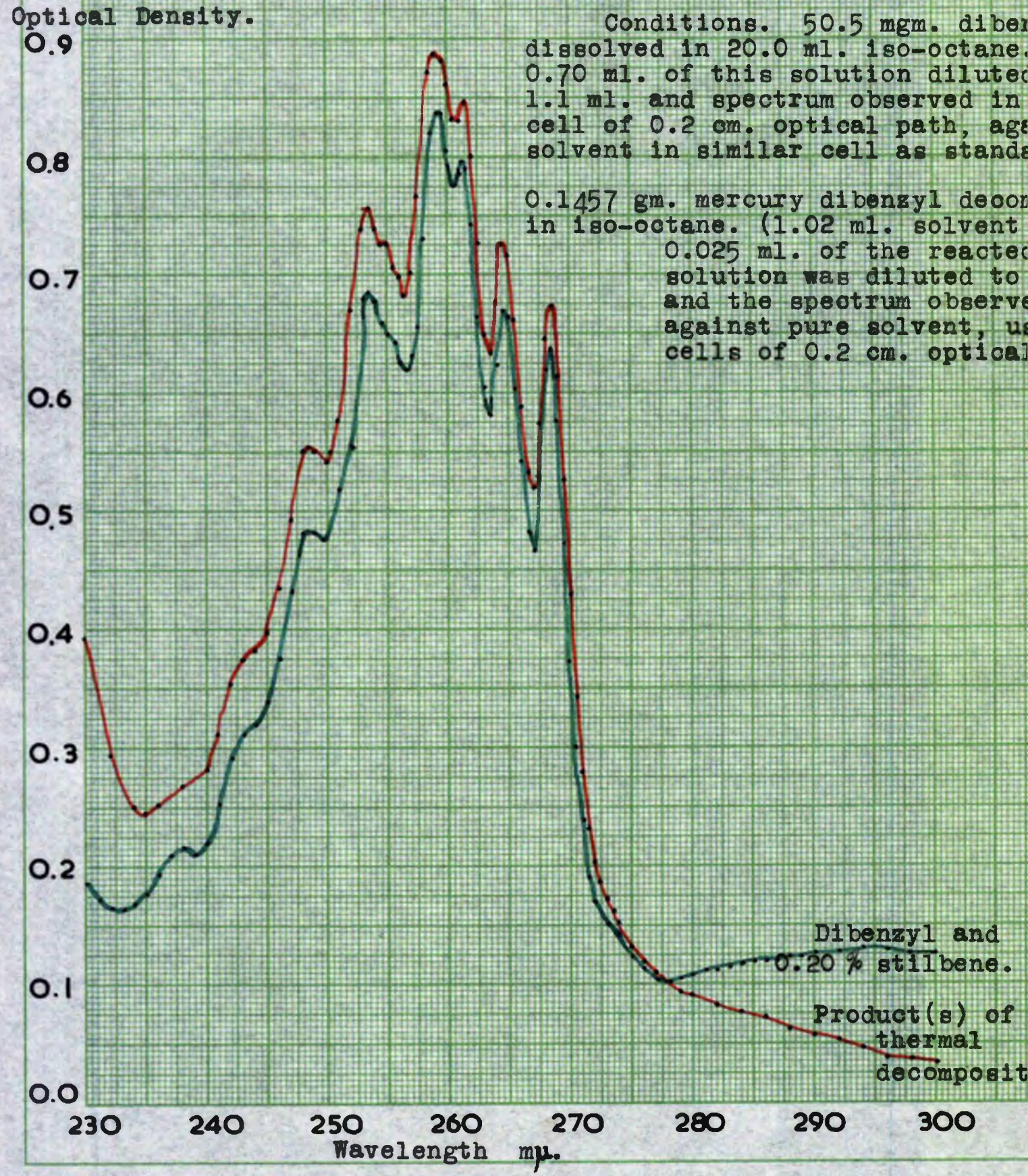


Graph 13. The plot of the data from Table 7 .

Table 7. Data for Experiments with Mercury Dibenzyl in iso-octane.

Expt. No.	°C.	°T.	$10^4/T$	$\log_{10}k_1$ 272 mμ min^{-1}	$\log_{10}k_1$ 290 mμ min^{-1}	Approx. final % decomp.
2/I	147.0	420.2	23.80	$\bar{3}.845$	$\bar{3}.840$	98
3/I	146.5	419.7	23.83	$\bar{3}.835$	$\bar{3}.834$	90
4/I	146.5	419.7	23.83	$\bar{3}.834$	$\bar{3}.848$	90
5/I	137.0	410.2	24.38	-	-	-
6/I	139.1	412.3	24.25	$\bar{3}.386$	$\bar{3}.371$	60
7-8/I	130.9	404.1	24.74	$\bar{4}.997$	$\bar{4}.972$	40
9-10/I	120.1	393.3	25.43	$\bar{4}.444$	$\bar{4}.413$	46
15/I	138.7	411.9	24.28	$\bar{3}.438$	$\bar{3}.437$	72
16/I	100.8	374.0	26.74	$\bar{5}.378$	$\bar{5}.415$	39
17/I	129.5	402.7	24.84	$\bar{4}.999$	$\bar{4}.997$	43
18/I	146.8	420.0	23.81	$\bar{3}.815$	$\bar{3}.814$	89
19/I	146.6	419.8	23.82	$\bar{3}.863$	$\bar{3}.881$	85
20/I	139.4	412.6	24.24	$\bar{3}.500$	$\bar{3}.506$	67
21/I	100.9	374.1	26.73	$\bar{5}.365$	$\bar{5}.380$	5
22/I	139.3	412.5	24.24	$\bar{3}.495$	$\bar{3}.471$	65
23/I	100.9	374.1	26.73	-	-	-
24/I	99.8	373.0	26.81	$\bar{5}.429$	$\bar{5}.421$	42
25/I	139.8	413.0	24.21	$\bar{3}.482$	$\bar{3}.449$	80
26/I	138.8	412.0	24.27	$\bar{3}.441$	$\bar{3}.416$	75
27/I	156.8	430.0	23.26	$\bar{2}.326$	$\bar{2}.307$	55
28/I	156.8	430.0	23.26	$\bar{2}.326$	$\bar{2}.310$	82
29/I	112.9	386.1	25.90	$\bar{4}.062$	$\bar{4}.030$	57
30/I	112.8	386.0	25.91	$\bar{4}.038$	$\bar{4}.019$	57
32/I	138.7	411.9	24.28	$\bar{3}.416$	$\bar{3}.364$	73

Graph 14. The ultra-violet spectra, in iso-octane as solvent of dibenzyl (contaminated with a little stilbene) and the organic product(s) from the thermal decomp of mercury dibenzyl in iso-octane.



Graph 13 shows the plot of $\log_{10} k_1$ against $10^3/T$, using the data for wavelength 272 mμ from Table 7.

The equation

$$k_1 = 10^{16.25} . \exp(-38,800/RT) \text{ sec.}^{-1}$$

represents the variation of the first order velocity constant with temperature, and was obtained from the average of the log k_1 data for wavelengths 272 mμ and 290 mμ (excluding the values for 24/I) using the method of least squares (41).

(31) <u>The Products of the Thermal Decomposition of Mercury Dibenzyl in iso-octane solution.</u>

The products of the thermal decomposition of mercury dibenzyl in iso-octane have already been indicated to be mercury and dibenzyl. The gravimetric method of analysis established 100% yield of mercury. (See pages 34, 35).

The solutions produced during the complete decomposition of mercury dibenzyl in Experiments 11/I, 12/I, 42/I and 43/I were analysed by determination of their ultra-violet absorption spectra. The results for Experiment 11/I are indicated in Graph 14. It is seen that the spectrum of the product is practically identical with that for an authentic sample of dibenzyl which was known to contain approximately 0.2 mole % of an impurity, stilbene, formed during the synthesis of the dibenzyl.

The results for the quantitative determination of dibenzyl in these four solutions are indicated in the Table

below. For these analyses, the standard dibenzyl spectrum in Graph 14 was corrected for the stilbene content, and for Experiment 11/I an allowance was made for the residual undecomposed mercury dibenzyl, the quantity of which (0.57%) was calculated from the known rate constant for the decomposition.

Expt. No.	gm. mercury dibenzyl	mgm. dibenzyl found	Approx. % recovery
11/I	0.1457	81	117
12/I	0.4048	230	120
42/I	0.01017	5.6	115
43/I	0.01373	7.2	109

Several possible sources of error might have contributed to give these high recoveries of dibenzyl.

An examination of the errors associated with the experimental techniques suggested that they could not have been responsible for these high yields of dibenzyl. In particular, the errors involved in the weighing of samples, the preparation and dilution of solutions for optical analyses, and the analyses themselves were examined and were shown to be small. The maximum error found from all these sources was never greater than 2-3% for repeat analyses of a given material.

The extinction coefficients obtained from the dibenzyl spectrum, Graph 14, after the correction for the stilbene content, were less than the corresponding values obtained from published data (42), except in the wavelength region 260-265 mμ, where good agreement was attained. The analyses of Experiments 42/I and 43/I based on data from within this

spectral region gave dibenzyl recoveries 4-5% lower than those quoted above, which were obtained from data over the wavelength range 245-270 mμ. However, as the published data did not show resolution of the two peaks at 259-261.5 mμ, it may itself have been slightly in error.

Because of the relatively low extinction coefficients for dibenzyl, the presence in the mercury dibenzyl of a small amount of an impurity which possessed high extinction coefficients and which remained unaltered during the thermal decompositions could account for the enhanced optical densities of the product spectra. Thus, 0.25-0.5 mole % of such an impurity, having extinction coefficients equal to those for mercury dibenzyl, would have increased the optical densities of the product spectra sufficiently to suggest 110-120% recovery of dibenzyl.

The most likely impurity would have been benzyl mercury chloride, which has an absorption maximum at 245 mμ ($\log \epsilon = 4.16$) (43). It was over the region 240-250 mμ that the ratios of the optical densities from the published data on dibenzyl to those for the products were at a maximum, thus indicating the presence in the product of a second component which had an absorption maximum in this region.

From the dibenzyl recoveries quoted in the Table above, it is seen that the impurity effect caused less error in Experiments 42/I and 43/I, which were performed with the vacuum recrystallised mercury dibenzyl, suggesting that the reactant in these experiments was of greater purity that that used in the earlier experiments.

The Ostwald solubility coefficient for oxygen dissolved in iso-octane is quoted as 0.37 at 0-25°C. by Seidel and Linke (44), which is small enough to indicate that insufficient oxygen remained in the reaction vessels after the degassing procedures to form significant quantities, say 0.5 mole %, of intensely absorbing materials by direct interaction with mercury dibenzyl or its decomposition products. For example, approximately 2 ml. of oxygen, measured at 1 mm. pressure and room temperature, would have been required for the formation of such quantities of side products during Experiment 42/I and 43/I. Considerably better vacua, i.e. 10^{-3}-10^{-4} mm. mercury, were always attained during the degassing before vessels were sealed.

The effect of large amounts of oxygen on the decomposition of mercury dibenzyl is discussed in the next section. The products obtained, which were not identified, had absorption maxima at 230 mμ and not at 240-250 mμ as would be required to explain the high recoveries of dibenzyl during the four experiments reported above.

These high analytical results could not be attributed to the optical absorption caused by solution of the mercury in the iso-octane. The absorption maxima for solutions of mercury in hydrocarbon solvents occur at approximately 255-257 mμ (38), (45), not at 240-250 mμ as required, and during these four experiments such an effect would have caused a maximum increase of only about 2% in the optical density values over the wavelength region 255-257 mμ, and thus would not have been

detected readily.

The presence of products of an unsaturated character might also account for the enhanced optical densities obtained in these dibenzyl spectra. Evidence from several sources, however, including some of the earlier published work with mercury dibenzyl mentioned on pages 26, 27 and 28, suggests that benzyl radicals produced at moderate temperatures do not readily attack saturated paraffin solvents to produce detectable quantities of unsaturated products, but instead they dimerise (46), (47).

Thus, the most likely source of error responsible for these high recoveries of dibenzyl would have been an impurity, suspected to be 0.25-0.5 mole % of benzyl mercury chloride, present in the vacuum recrystallised mercury dibenzyl. Errors of secondary importance occurred because the standard dibenzyl absorption curve required corrections for the stilbene present.

The melting point of the organic product from the total decomposition of mercury dibenzyl in iso-octane was determined with a sample of the material which had been sublimed at 52°C. in air.

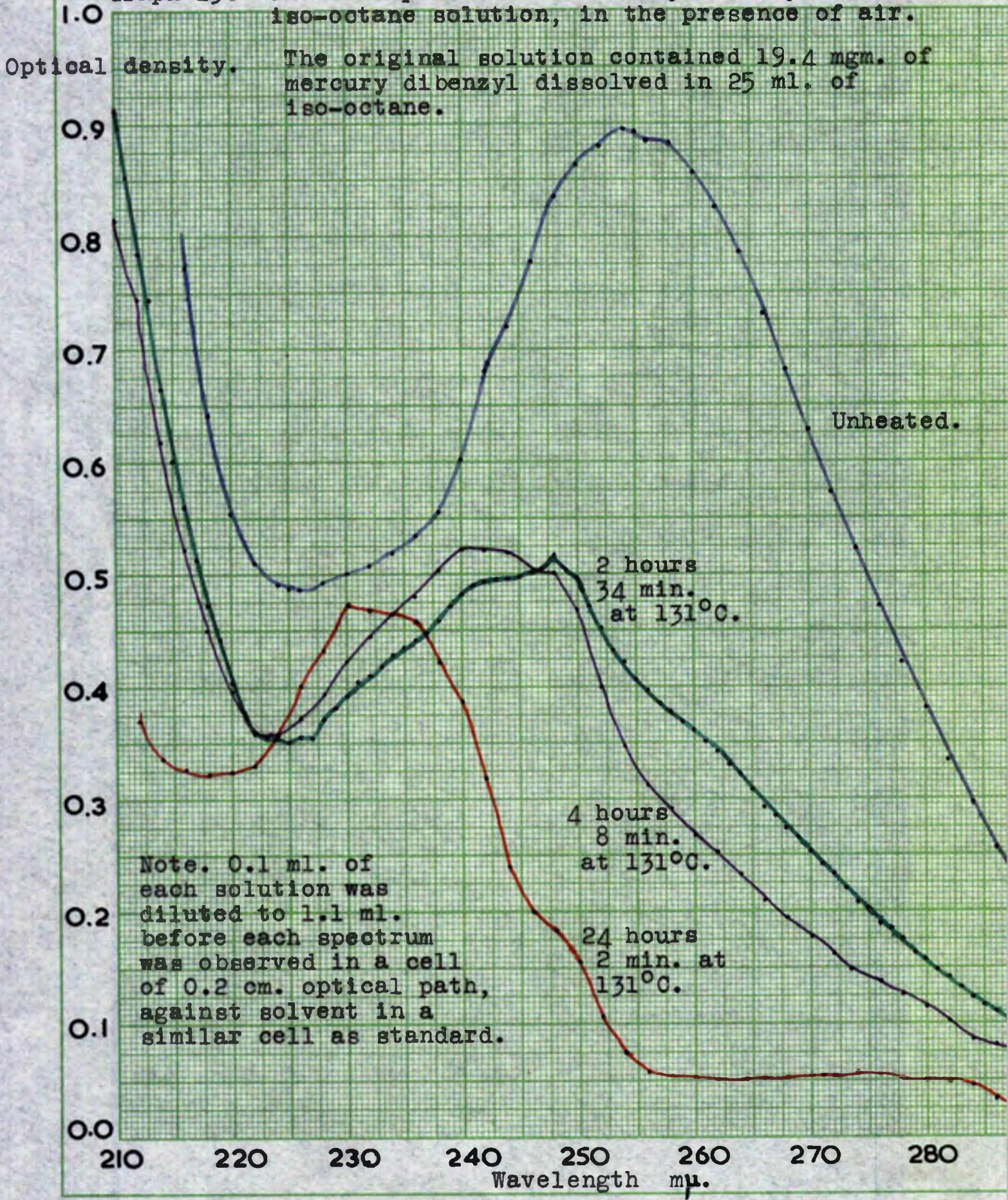
M.pt. of the sublimed sample 51.7-52.5°C. (corrected).

M.pt. of dibenzyl 52.00°C. (48).

(The melting points of unsublimed samples were always low and of wide range. This was attributed to the tenacious retention of the solvent by the crystals).

Dibenzyl was concluded to be the only significant organic product formed during the decomposition of mercury dibenzyl.

Graph 15. The decomposition of mercury dibenzyl in iso-octane solution, in the presence of air.



(3j) The Reactions of Mercury Dibenzyl in iso-octane, in the presence of air.

An observation made during Experiment 9-10/I concerning the possible effect of oxygen on the thermal decomposition of mercury dibenzyl dissolved in iso-octane has been referred to above on page 56.

In order to ascertain if oxygen did affect this thermal decomposition, Experiments 13/I and 14/I were performed with solvent which had not been degassed.

Clean reaction vessels, which had been prepared in the usual manner, were filled with 0.51 ml. of a solution of mercury dibenzyl in iso-octane and then sealed, without either degassing the solvent or removal of air from the vessels.

The vessels were inserted in the thermostat set at 131°C.. After known periods of immersion, they were removed and their contents were analysed by ultra-violet absorption spectroscopy in the usual manner. In addition, the complete ultra-violet spectra was obtained for some of the solutions.

The results which were obtained are indicated in Graph 15. These data indicated that the presence of air in the reacting system caused considerable changes in both the kinetics of the decomposition and the products obtained.

This effect was not investigated further, but in all subsequent experiments extra care was taken to ensure the removal of traces of air from the vessels before they were sealed.

THE DETAILED MECHANISM OF THE THERMAL DECOMPOSITION OF MERCURY DIBENZYL IN SOLUTION IN ISO-OCTANE.

(1) The use of diphenyl picryl hydrazyl.

To study the fine detail of the liquid phase thermal decomposition of mercury dibenzyl, and in particular to establish whether or not free benzyl radicals were produced during the decomposition, it was planned to carry out the decomposition of the mercury dibenzyl in the presence of diphenyl picryl hydrazyl (D.P.P.H.), which being itself a stable free radical, R-, might be expected to react in the following manner with any benzyl radicals, Bz-, produced in the system :-

$$R- + -Bz \rightarrow R-Bz \quad .$$

Several workers have used D.P.P.H. for similar purposes (49, 50), but no work at temperatures above 80°C. appears to have been published.

D.P.P.H. was prepared by Goldschmidt and Renn's method (51). The product was recrystallised from chloroform and vacuum dried.

The material was dissolved in spectroscopic iso-octane. Portions of the solution were placed in cleaned reaction vessels of the type described in Section (3e), page 61, and the liquid was degassed three times. The vessels were then sealed and inserted in the thermostat at 137.2°C. A rapid reaction occurred at this temperature, and the product was identified from its ultra-violet absorption spectrum as

diphenyl picryl hydrazine (50).

A similar reaction occurred in spectroscopic iso-octane which had been kept over fresh vacuum distilled sodium. It was thus concluded that the D.P.P.H. was not reacting with any adventitious water which might have been present in the solvent (50). Thus, the D.P.P.H. could have reacted with either the solvent, S :-

$$R- + S \longrightarrow R-H + \text{other products},$$

or, since the purity of the D.P.P.H. was not rigorously investigated, with some impurity I :-

$$R- + I \longrightarrow R-H + \text{other products}.$$

Concurrently with this work with D.P.P.H., attempts were made to prepare di-substituted mercury dibenzyls. One of these was successful, as indicated below, and the D.P.P.H. method was not developed further.

(2) <u>The Use of a di-substituted Mercury Dibenzyl</u>.

A second approach to the study of the fine detail of the decomposition of mercury dibenzyl would be to carry out the decomposition of the material in the presence of a suitably marked mercury dibenzyl. In this manner, it was hoped that a distinction could be made between the following possible reaction schemes :-

(a) Radical Decomposition.

$$Bz\text{-}Hg\text{-}Bz \longrightarrow Bz\text{-}Hg\text{-} + \text{-}Bz \longrightarrow Bz\text{-} + Hg + \text{-}Bz$$

$$Bz\text{-} + \text{-}Bz \longrightarrow Bz\text{-}Bz$$

$$Bz'\text{-}Hg\text{-}Bz' \longrightarrow Bz'\text{-}Hg\text{-} + \text{-}Bz' \longrightarrow Bz'\text{-} + Hg + \text{-}Bz'$$

$$Bz'\text{-} + \text{-}Bz' \longrightarrow Bz'\text{-}Bz'$$

$$Bz\text{-} + \text{-}Bz' \longrightarrow Bz\text{-}Bz'$$

(b) Non-radical Decomposition.

$$Bz\text{-}Hg\text{-}Bz \longrightarrow Hg + Bz\text{-}Bz$$

$$Bz'\text{-}Hg\text{-}Bz' \longrightarrow Hg + Bz'\text{-}Bz'$$

(c) A Bimolecular Decomposition.

Cross product formation by a mechanism of the type :-

$$\begin{matrix} Bz\text{-}Hg\text{-}Bz \\ + \\ Bz'\text{-}Hg\text{-}Bz' \end{matrix} \longrightarrow \begin{matrix} Hg \\ Bz'\text{-}Bz \\ Hg \end{matrix} \quad Bz\text{-}Bz'$$

might have been considered if it were not that the decomposition of the mercury dibenzyl had already been shown to follow a first order law.

Thus, the presence or absence of the mixed dibenzyl in the products of the reaction would indicate which was the correct reaction scheme.

Assuming that the radical mechanism (a) is correct, this type of investigation would only be successful if the following conditions were fulfilled :-

(a) At the same temperature, the Hg-C bonds of both compounds must be broken at comparable rates, and preferably nearly equal rates.

(b) The radicals formed must be able to diffuse away from the site of the decomposition and the "cage"

of solvent molecules must not exercise a dominating influence favouring the recombination of the two radicals produced from a given molecule.

(c) The dimerisation process must not discriminate strongly against the formation of the mixed dibenzyl, Bz-Bz'.

(d) An analytical procedure has to be devised which will detect and estimate the cross product, Bz-Bz'.

Experiments with the chosen mercury dibenzyls can determine their separate decomposition rates and so clarify (a), and (d) is also subject to experimental test by investigations with synthetic mixtures. But if the final experiments do not yield the cross product, (b) or (c) or both could be a possible cause.

(2a) Di-substituted Mercury Dibenzyls - Mercury Di-(p-nitrobenzyl).

It was considered that mercury di-(p-nitrobenzyl) would have been a suitable di-substituted compound with which to have performed these experiments.

Several possible methods to synthesise this compound were, however, unsuccessful.

Attempt 1.

Attempts to convert p-nitrobenzyl chloride to the Grignard compound, using the usual reaction conditions, were not successful; thus a method of preparation analogous to that used for mercury dibenzyl could not be employed.

Attempt 2.

Maynard (52) had prepared benzyl mercuric iodide in 94% yield by the interaction of benzyl iodide and specially prepared mercurous iodide during 3 hours heating in a sealed vessel at

50°C., under ultra-violet radiation.

p-nitrobenzyl chloride was twice recrystallised from methyl alcohol. The purified material was converted in 91% yield to p-nitrobenzyl iodide by Finkelstein's method (53). (m.pt. of product recrystallised from ethyl alcohol 126.4-127.1°C.(corrected). Literature m.pt. 127°C. The material sublimed in air at temperatures above 120°C.)

5.2 gm of the p-nitrobenzyl iodide was sealed under high vacuum with 13 gm of specially prepared mercurous iodide, and the vessel heated at 150°C. for 20 minutes, under ultra-violet radiation. The hot semi-liquid material rapidly solidified. The vessel was opened, and the solid was extracted with 30 ml. of boiling chloroform, and the solution was filtered off. The red filtrate was discarded. The residue was treated with four successive portions each of 30 ml. of boiling acetone and filtered. (In subsequent preparations Soxhlet extraction with refluxing acetone was found to be more effective). The combined filtrates were evaporated to 50 ml. and allowed to cool. The fine pale-yellow matted crystalline precipitate was filtered off. The yield was 2.7 gm. or 29%.

A small quantity of the product was recrystallised from hot acetone. The crystals were washed with cold acetone and vacuum dried. M.pt. 174.0-175.0°C. (corrected).

Analysis of this material.

This yellow product, m.pt. 174.0-175.0°C., suspected to be p-nitrobenzyl mercury iodide, was analysed by the iodine

method of Whitmore and Sobatzki (36), (see page33), with the results shown in the Table below.

20.00 ml. of iodine solution were equivalent to 20.20 ml. of 0.0995 N thiosulphate solution			
gm. of sample refluxed with 20.00 ml. I_2	ml. thio. required for the excess I_2	thio. equiv. to I_2 used by sample.	calculated M.W. assuming 100% purity.
0.1252	14.90	5.30	475
0.0976	15.55	4.65	422
0.1118	15.15	5.05	445
0.0937	16.00	4.20	449
Molecular weight of p-nitrobenzyl mercury iodide			463.6

From the agreement between the expected and experimental molecular weights, it was concluded that the formula of the yellow material was $NO_2(C_7H_6)HgI$. The position of entry of the mercury atom into the molecule was decided by the following method.

The solutions from the four analyses were combined and the chloroform was separated from the aqueous layer. The organic phase was dried with anhydrous calcium chloride and then filtered. The chloroform was evaporated, leaving pale yellow needle-shaped crystals which melted at 120.3-125.5°C. (corrected). (A sublimate was observed at temperatures above 100°C.).

These crystals were treated in the following manner. They were dissolved in chloroform/ether mixture and a little aqueous thiosulphate solution was added to discharge the iodine colour. The phases were separated, and the organic phase was dried with anhydrous sodium sulphate. After filtration, the filtrate was

evaporated to dryness, and the crystals which were obtained were washed with ethyl alcohol. The crystals were recrystallised from ethyl alcohol. A small quantity of the final product was sublimed at 115°C./1 mm. These sublimed crystals melted at 125.5-126.5°C. (corrected). If the starting material for the iodine analyses had been p-nitrobenzyl mercury iodide, then the final product would have been p-nitrobenzyl iodide. The literature m.pt. of p-nitrobenzyl iodide is 124°C.(53).

Thus it was established that the organo-metallic compound prepared was in fact the p-nitrobenzyl mercury iodide desired.

The Attempted Preparation of Mercury Di-(p-nitrobenzyl).

Several attempts to convert the p-nitrobenzyl mercury iodide to mercury di-(p-nitrobenzyl) by a method similar to that used for the preparation of mercury dibenzyl failed to give the product expected. Evaporation of the purified chloroform extracts (see STAGE 3, page 30) yielded two coloured crystalline components, one red and one pale yellow.

The red component was most probably mercuric iodide, as it was soluble in aqueous potassium iodide solutions and then passage of hydrogen sulphide produced a black precipitate.

The m.pt. of the yellow material after two successive recrystallisations from ethyl alcohol, during which it formed needles and then plates, was 48-52°C. (uncorrected).

As a result of subsequent experiments with the sodium iodide method of preparation, which are described below, it was suspected that this pale yellow material was p-nitrotoluene.

The m.pt. of an authentic sample of p-nitrotoluene was found to be 52.5°C. (uncorrected). The crystals were observed to sublime at temperatures above 40°C. The mixed m.pt. of the pale yellow product (m.pt. 48-52°C.) with the authentic p-nitrotoluene was 48-52.5°C.

Thus, it was concluded that the product, instead of being mercury di-(p-nitrobenzyl), was p-nitrotoluene.

Attempt 3.

Whitmore was able to prepare several mercury dialkyl and diaryl compounds by the reaction

$$2\ ArHgX + 2\ NaI \longrightarrow Ar_2Hg + Na_2HgI_2X_2 \ ,$$

performed in 95% ethyl alcohol as solvent (36).

In an initial experiment, 0.51 gm. of p-nitrobenzyl mercury iodide was added with 1.78 gm. anhydrous sodium iodide to 10 ml. ethyl alcohol. The solution became bright yellow. The mixture was refluxed for 5 minutes, and a precipitate of mercury was produced.

A second experiment was performed with similar weights of reactants, each dissolved separately in 125 ml. of alcohol. Addition of a small volume of either solution to a large volume of the other produced flashes of deep yellow colour which disappeared on thorough mixing. The final solution had a pale yellow colour. The solution was maintained at room temperature. Passage of hydrogen sulphide through a small sample of the solution gave a black precipitate. (A test solution of

p-nitrobenzyl iodide in alcohol gave no such precipitate with hydrogen sulphide).

It was concluded that a reaction had occurred. A product was isolated in the following manner :-

Addition of water gave a milky-white solution. Chloroform was added and the mixture shaken. The chloroform layer cleared slowly when the mixture was allowed to stand. The lower layer was very pale brown; it was removed and the solvent was allowed to evaporate at room temperature. After four days the solution yielded long pale yellow needles whose m.pt. was 46.5-51°C. (uncorrected).

This product, suspected at this stage to be mercury di-(p-nitrobenzyl), was analysed by the iodine method. 0.0902 gm. of the product was refluxed for 3½ hours with 20.00 ml. of iodine solution (which was initially of strength equivalent to 20.20 ml. of 0.0995 N thiosulphate solution) together with 5 ml. of chloroform and 25 ml. of distilled water. The refluxed solution contained unreacted iodine equivalent to 20.0 ml. of 0.0995 N thiosulphate solution. (The expected thiosulphate titre for 0.0902 gm. of material having the formula $(NO_2.C_6H_4.CH_2)_2Hg$ was 12.5 ml.).

The product was concluded to be practically devoid of organo-mercury compounds, and it might have been the same product as had been obtained in the experiments reported immediately above (Attempt 2.), because of the similar m.pts. of the two products.

Possible products would have included :-

p,p'-dinitro dibenzyl
p-nitrotoluene.

Of these, the first has a m.pt. of 180.5°C. and is clearly inadmissible. The second has a literature m.pt. of 51.5°C., which is close to the value 46.5-51°C. (uncorrected) observed for the product. The ultra-violet spectra of the product and an authentic sample of p-nitrotoluene were sufficiently similar to suggest a close relation between the structures of the two compounds.

Again it was concluded that, instead of mercury di-(p-nitrobenzyl), p-nitrotoluene was produced.

Attempt 4.

Kharasch (54) reported the isolation of mercury di-(2,4-dinitrobenzyl) from the products of the thermal decomposition of the mercuric salt of 2,4-dinitrophenyl acetic acid, but he did not quote any yields.

A similar decomposition might occur with the mercuric salt of p-nitrophenyl acetic acid.

p-nitrophenyl acetic acid, prepared by the ice-cold nitration of phenyl acetic acid (55), was converted to the mercuric salt with mercuric acetate, using Kharasch's method (54).

When the mercuric salt of the acid was heated to 190°C., a gas was evolved and a clear yellow product remained; this product was completely soluble in acetone, but no crystalline material could be isolated. Quantitative experiments showed that the gas evolution was only 1-2% of that expected.

Prolonged heating of the mercury salt of the acid at 155°C. gave a small quantity of mercury and a product which, when recrystallised from acetone, melted over the range 190-200°C. (uncorrected). (One possible product would have been 4,4'-dinitro dibenzyl which has literature m.pts. of 178°C., 180-182°C., 180.5°C. and 182°C.).

Because of the difficulties encountered during this reaction, an attempt was made to repeat Kharasch's preparation of mercury di-(2,4-dinitrobenzyl).

Heating the pale yellow mercuric salt of 2,4-dinitrophenyl acetic acid at 180°C. for 30 minutes gave a red solid in the reaction vessel. (The loss of weight was 88% of that expected).

The red product melted at 190°C. (uncorrected) with evolution of a gas. Boiling the product with acetone, filtering and drying, gave a material of m.pt. 210°C. (uncorrected). (A gas was still evolved).

This material was dissolved in pyridine and reprecipitated by the addition of ligroin. The red solid was filtered off and dried. M.pt. 225-230°C. (corrected). Kharasch's value of the m.pt. of mercury di-(2,4-dinitrobenzyl) was 235°C., with separation of mercury.

An analysis of 0.1180 gm. of this red crystalline product by Whitmore's method (see page 33) gave an iodine consumption equivalent to a compound, having 2 mercury-carbon bonds per molecule, of M.W. 579, or 3% higher than the calculated M.W. of mercury di-(2,4-dinitrobenzyl), 563.

It was thus apparent that the formation of the tetra-nitro mercury dibenzyl proceeded more readily than the formation of the required di-nitro compound.

It might be suggested that mercury di-(2,4-dinitrobenzyl) could be used as the second, marked, mercury dibenzyl, but the presence of two substituents in each phenyl group may considerably alter the Hg-C bond strength, and thus condition (a), page 77, would not be met. Unfortunately the material was too insoluble in iso-octane and other organic solvents for this supposition to be readily investigated.

At this stage, considerable progress was being made with other syntheses, which are described below, and this decarboxylation method was not further investigated.

(2b) Di-substituted Mercury Dibenzyls - Mercury Di-(p-chlorbenzyl).

Mercury di-(p-chlorbenzyl) was prepared from p-chlorbenzyl chloride via the Grignard compound by a procedure analogous to that described for the preparation of mercury dibenzyl.

The preparation of the intermediate p-chlorbenzyl mercury chloride.

The p-chlorbenzyl chloride was purified before use by the method of fractional freezing, rejecting the liquid phase. The preparation of the Grignard compound followed the method outlined for Stage 1 of the preparation of mercury dibenzyl, page 29.

The Grignard compound was converted to the required intermediate by the method given by Gilman and Brown (33) in an apparatus filled with oxygen-free dry nitrogen. The solvent of

the filtered Grignard solution was refluxed over a Soxhlet extraction cup which contained dry, finely powdered mercuric chloride until all the chloride had been extracted. A precipitate of the product formed. The addition of water and dilute hydrochloric acid to the ethereal suspension of the intermediate resulted in an additional fine white precipitate. The ether was distilled, and the fine white solid filtered off, dissolved in boiling ethyl alcohol and the solution was allowed to cool. Very fine needle crystals were obtained, which yielded a matted crystalline mass on filtration. The yield was 19.6 gm. from 16.7 gm. p-chlorbenzyl chloride, or 52%.

The Analysis of this Intermediate.

A portion of this crude p-chlorbenzyl mercury chloride was recrystallised for analysis from hot ethyl alcohol, and then vacuum dried. M.pt. of the product was 145.0-147.0°C. (corrected)*. (A sublimate was observed at temperatures just below the m.pt.).

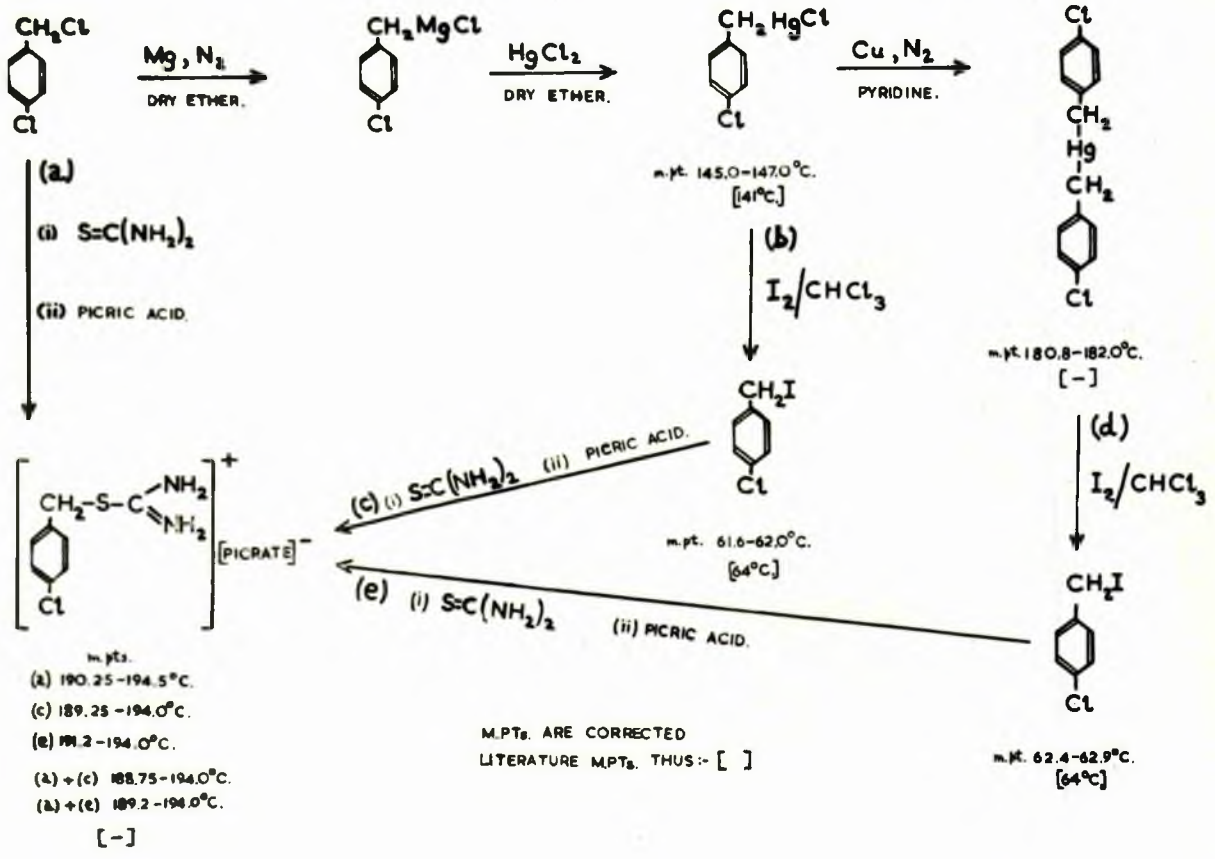
Four analyses were performed with this material, using the iodine method described on page 33. The results are given in the Table below.

20.00 ml. iodine solution were equivalent to 42.10 ml. of 0.0477 N thiosulphate solution.			
Gm. of sample refluxed with 20.00 ml. I_2	ml. thio. reqd. for excess I_2	thio. equiv. to I_2 used by sample	% purity
0.1357	26.40	15.7	99.9
0.1123	29.70	12.4	95.3
0.1315	26.70	15.4	101.1
0.1073	29.50	12.6	101.3

* Literature m.pt. of p-chlorbenzyl mercury chloride 141°C. (56).

FIGURE 22.

Fig. 22.



The preparation of mercury di-(p-chlorbenzyl), and degradation of the material to ascertain the structure.

The chloroform layer from a subsequent iodine analysis with this intermediate was separated, dried with anhydrous sodium sulphate, and the chloroform was evaporated. Needle crystals were obtained which melted at 48.1-60.5°C. (corrected). The material was sublimed in air at 60°C., and the sublimate melted at 61.6-62.0°C. (corrected). A second sublimation did not raise or sharpen this m.pt. (The literature m.pt. of p-chlorbenzyl iodide is 64°C.). Reaction (b) in Fig. 22 refers to this analysis.

For better identification, these crystals were converted to the S-(p-chlorbenzyl) iso-thiuronium picrate by the method described by Vogel (57). The picrate was recrystallised twice from ethanol and dried. M.pt. 189.25-194.0°C. (corrected). Reaction (c) in Fig. 22 refers to the preparation of this picrate.

A sample of the same picrate, prepared from authentic p-chlorbenzyl chloride, was recrystallised twice from methanol and dried. This picrate melted at 190.25-194.5°C. (corrected). Reaction (a) in Fig. 22 refers to the formation of this material.

The mixed m.pt. between samples of these two picrates was 188.75-194.0°C. (corrected).

<u>The conversion of the intermediate to mercury di-(p-chlorbenzyl).</u>

Oxygen-free, dry nitrogen was passed through pyridine containing a suspension of copper bronze. On the addition of the p-chlorbenzyl mercury chloride, which dissolved, a slight

green colour developed. The reaction mixture was warmed, and then allowed to stand overnight at room temperature under an atmosphere of nitrogen. A dark green solution was obtained, together with a mass of needle crystals. Dilute sulphuric acid (2 N) was added until no further precipitation resulted. The mixture was filtered, and the solid was extracted with portions of boiling chloroform. The combined chloroform solutions were washed twice with 2 N. sulphuric acid, twice with 2 N. ammonia solution and twice with distilled water. The solution was then dried with anhydrous sodium sulphate. The volume of the clear, light brown solution was reduced to 60 ml., and then decolourised with charcoal and allowed to crystallise. The crystals were filtered off and vacuum dried. The yield was 1.62 gm. from 8.00 gm. of p-chlorbenzyl mercury chloride and 15 gm. of copper bronze, or 32%.

The m.pt. of this material in air was 155.5-166.9°C. (corrected). This wide range of m.pt. was very unexpected, especially in view of the purity of the product (which is reported in the next section), and it was traced to the reaction of the material with the air at these high temperatures. The m.pt. of the material under vacuum conditions is reported below.

The analysis of the mercury di-(p-chlorbenzyl).

Several analyses of the material, which was assumed to be mercury di-(p-chlorbenzyl), were performed by the iodine method. The results obtained are indicated in the Table overleaf. Reaction (d) of Fig. 22 refers to these analyses.

For (i) and (ii), 20.00 ml. of iodine solution were equivalent to 20.10 ml. of 0.0988 N thiosulphate solution.
For (iii) and (iv), 20.00 ml. of iodine solution were equivalent to 44.30 ml. of 0.0448 N thiosulphate solution.

gm. of sample refluxed with 20.00 ml. I_2	ml. thio. required for the excess I_2	thio. equiv. to I_2 used by sample.	calculated M.W. assuming 100% purity.
(i) 0.1024	11.10	9.00	461
(ii) 0.1046	10.85	9.25	458
(iii) 0.0816	28.60	15.70	464
(iv) 0.1048	24.20	20.10	465
Molecular weight of mercury di-(p-chlorbenzyl)			451.8

The structure of the compound was indicated by the isolation, in the following manner, of p-chlorbenzyl iodide from the combined chloroform layers from these analyses.

The chloroform solution was washed with distilled water which contained a little thiosulphate solution to remove traces of free iodine formed by the decomposition of the iodide, and the water layer was separated. The chloroform solution was dried with anhydrous sodium carbonate, the solution was filtered, and the solvent was evaporated. Needle shaped crystals were obtained. A small portion of these were vacuum dried, and they melted at 61.5-62.4°C. (corrected). The material sublimed readily at temperatures above 60°C. A sublimed sample of these crystals melted at 62.4-62.9°C. (corrected). A second sublimation did not raise or sharpen the m.pt. (The literature m.pt. of p-chlorbenzyl iodide is 64°C.).

The remainder of these crystals were converted to the S-(p-chlorbenzyl) iso-thiuronium picrate (Reaction (e), Fig. 22). M.pt. of the picrate was 181.2-191.2°C. (corrected). The

picrate was recrystallised from ethanol, the crystals were washed twice with solvent and dried. M.pt. 191.2-194.0°C. (corrected). A mixed m.pt. of this picrate with the authentic picrate prepared from p-chlorbenzyl chloride (of m.pt. 190.25-194.5°C. (corrected), see page 88) was 189.2-194.0°C. (corrected).

The structure of this material was further indicated by the products of the thermal decomposition in degassed iso-octane as solvent. These were found to be mercury and p,p'-dichlordibenzyl, as reported below.

It was thus concluded that the desired mercury di-(p-chlorbenzyl) had in fact been prepared.

The purity of the material, as indicated by the iodine analyses reported on the previous page, was 98.1%, 98.7%, 97.4% and 97.1% for (i) to (iv) respectively.

The recrystallisation of the mercury di-(p-chlorbenzyl) from spectroscopic iso-octane under vacuum conditions.

In an attempt to purify the mercury di-(p-chlorbenzyl), the material was recrystallised from spectroscopic iso-octane (final solvent I) in a manner analogous to that described for mercury dibenzyl (page 58), except that no preliminary solubility experiments were performed because the material was not very soluble in iso-octane.

A hot saturated solution of the material in the degassed solvent was obtained under vacuum conditions in the vessel shown in Fig. 21. A considerable amount of the solid remained undissolved. The solution was filtered through the sintered

glass disc and allowed to cool. The crystals obtained were washed with the pure solvent, and then vacuum dried. They were kept in a brown bottle in darkness.

The m.pt. of these very fine needle crystals in air was 166-174.5°C. (corrected). Tiny dark specks were visible in the melt: these were most probably globules of mercury formed from the decomposition of the compound.

Samples of the vacuum recrystallised material were sealed in capillary tubes under conditions of high vacuo. The m.pt. of the material thus protected from atmospheric oxygen was 180.8-182.0°C. (corrected).

The purity of the recrystallised mercury di-(p-chlorbenzyl).

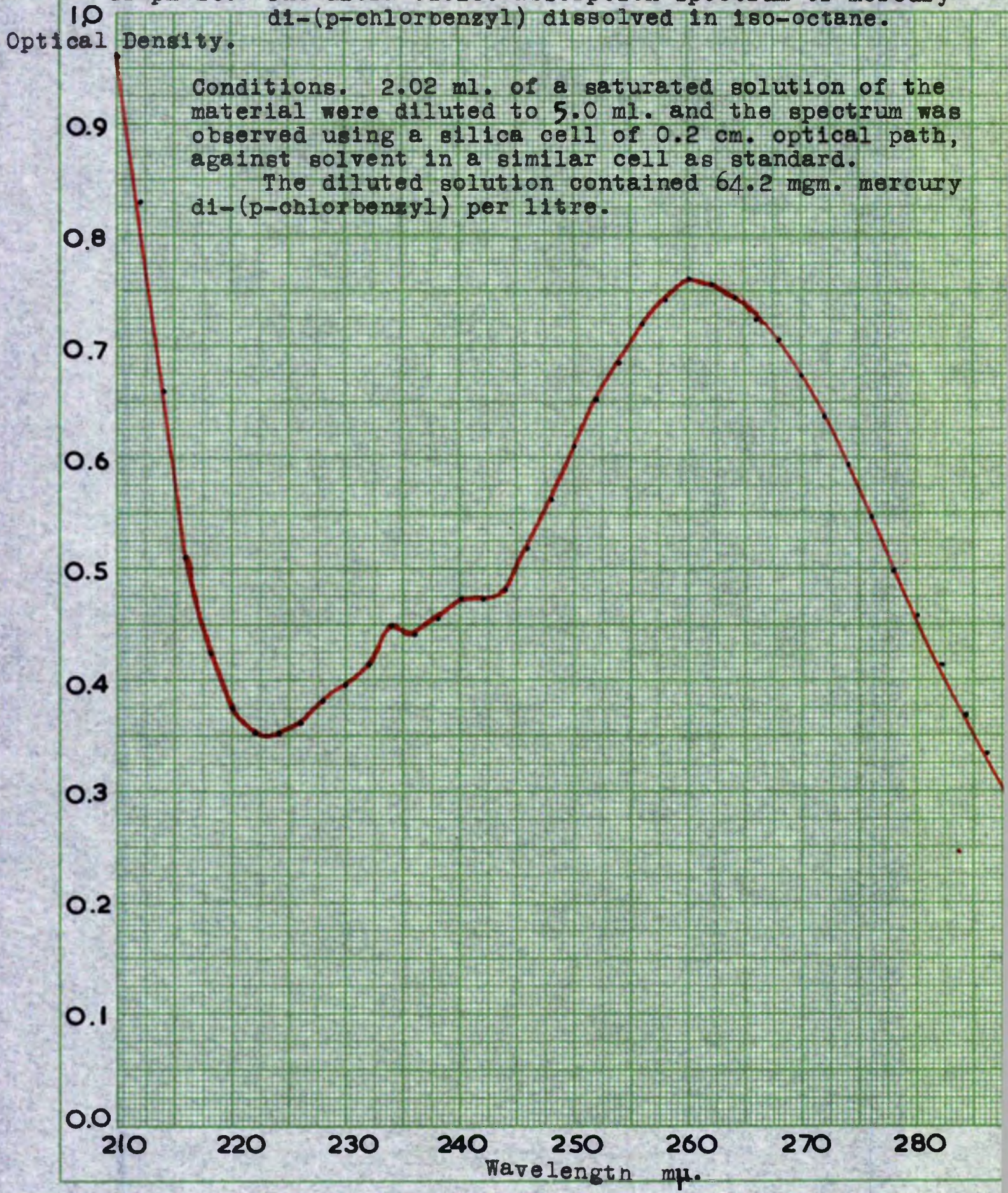
0.0514(4) gm. of the recrystallised material, when analysed by the iodine method, consumed iodine equivalent to 9.30 ml. of 0.0477 N thiosulphate solution, thus indicating a purity of 97.4% (with an estimated maximum error of ± 2%) for a compound of M.W. 451.8 having 2 Hg-C bonds per molecule.

Samples of the material were sealed, under vacuum conditions, in cleaned glass reaction vessels with thoroughly degassed iso-octane. These vessels were kept in the thermostat at 157.5°C. for 13 hours, 10 minutes. At the end of this period, the quantity of mercury in each vessel was estimated by the gravimetric method (see page 34). The results are indicated below.

Recovery of mercury from mercury di-(p-chlorbenzyl).

Vessel No.	gm. mercury compound	gm. mercury recovered	% mercury recovered
19	0.22333	0.09846	99.3
20	0.20893	0.09156	98.7
21	0.21295	0.09344	98.8

Graph 16. The ultra-violet absorption spectrum of mercury di-(p-chlorbenzyl) dissolved in iso-octane.



Conditions. 2.02 ml. of a saturated solution of the material were diluted to 5.0 ml. and the spectrum was observed using a silica cell of 0.2 cm. optical path, against solvent in a similar cell as standard.

The diluted solution contained 64.2 mgm. mercury di-(p-chlorbenzyl) per litre.

Some difficulties were experienced during these analyses because the mercury accumulated in tiny globules in each vessel. Most of these were collected on the filter discs. Some, however, remained firmly attached to the internal wall of each vessel. The amount of this residual mercury was determined by drying each vessel, whose outer surface had been carefully cleaned, in air to constant weight. Each vessel was then heated to volatilize any residual mercury, then cooled and reweighed. The loss in weight of each vessel was added to the weight of mercury collected from that vessel.

The recrystallised mercury di-(p-chlorbenzyl) was concluded to be at least 98.9% pure.

The spectral absorption of the mercury di-(p-chlorbenzyl).

Standard solutions of mercury di-(p-chlorbenzyl) in iso-octane were prepared in a manner similar to that described for the standard solutions of mercury dibenzyl.

The ultra-violet absorption spectrum of the mercury di-(p-chlorbenzyl) is shown in Graph 16.

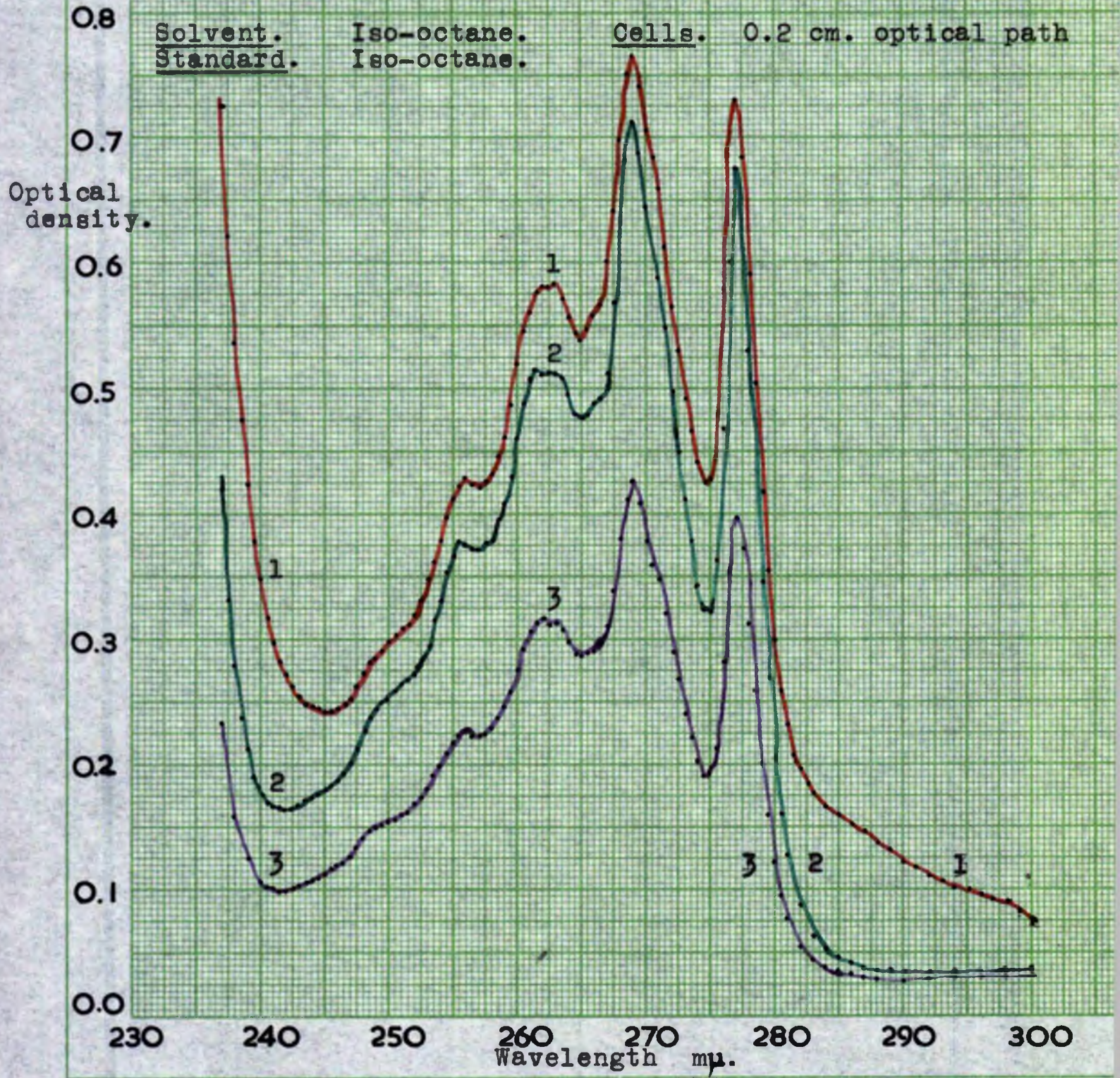
The intensity of this spectrum suggested that optical techniques could be employed to follow thermal decompositions of this material, and thus determine if this compound could be used as the marked mercury dibenzyl to investigate the detail of the mechanism of the thermal decomposition of the parent mercury dibenzyl as outlined on pages 76 and 77. The results of such experiments are reported below.

Graph 17. Spectra of samples of p,p'-dichlordibenzyl from:-

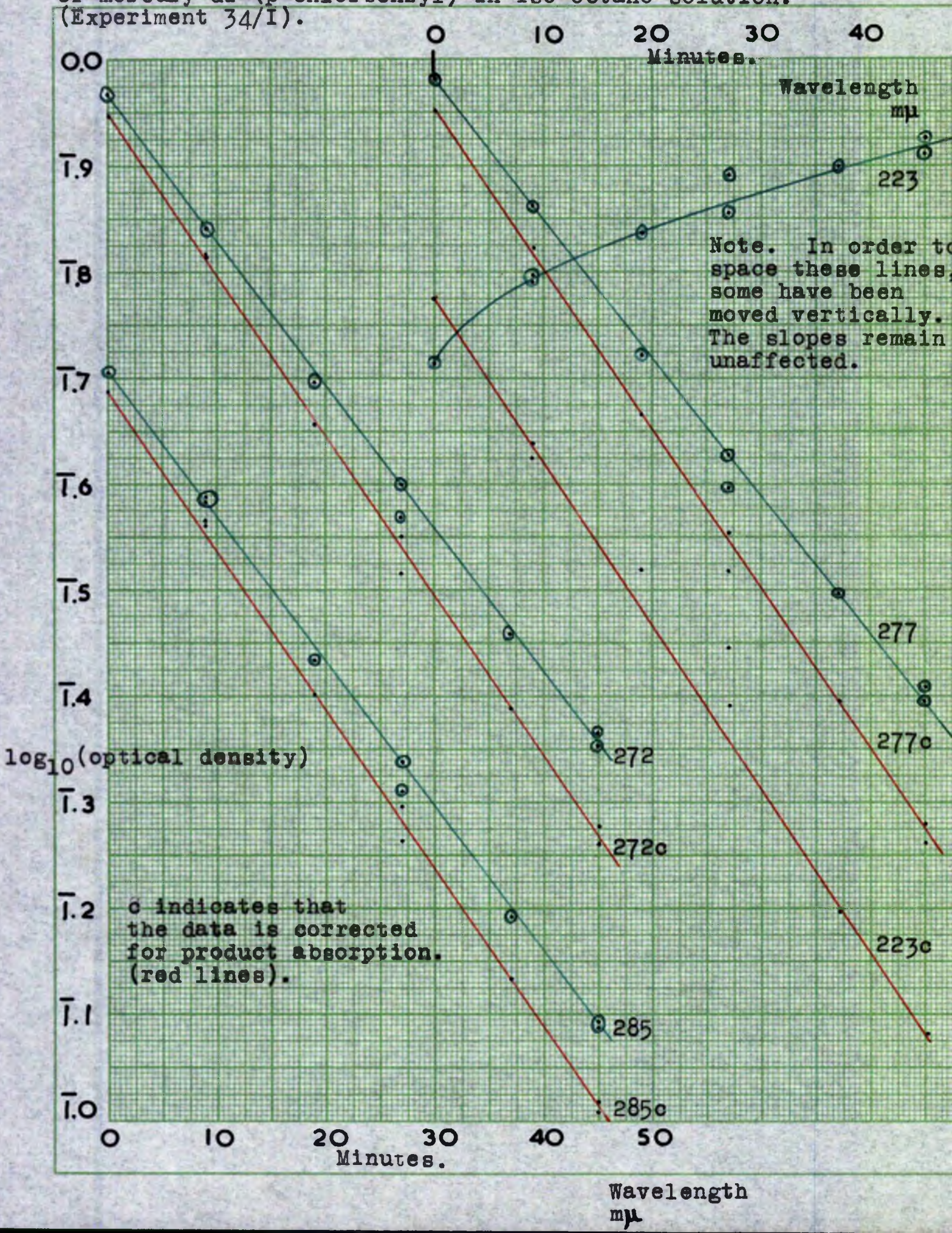
1. The thermal decomposition of mercury di-(p-chlorbenzyl), see page 94. (Red curve).
2. The Grignard synthesis, see page 110. (Green curve).
3. The catalytic hydrogenation of p,p'-dinitrodibenzyl, see page 113. (Purple curve).

Conditions. 1. 4.53 mgm. compound dissolved in 5.00 ml.
2. 4.82 mgm. compound dissolved in 5.00 ml.
3. 0.62 mgm. compound dissolved in 1.18 ml.

Solvent. Iso-octane. Cells. 0.2 cm. optical path
Standard. Iso-octane.



Graph 18. Typical experimental results for the decomposition of mercury di-(p-chlorbenzyl) in iso-octane solution. (Experiment 34/I).



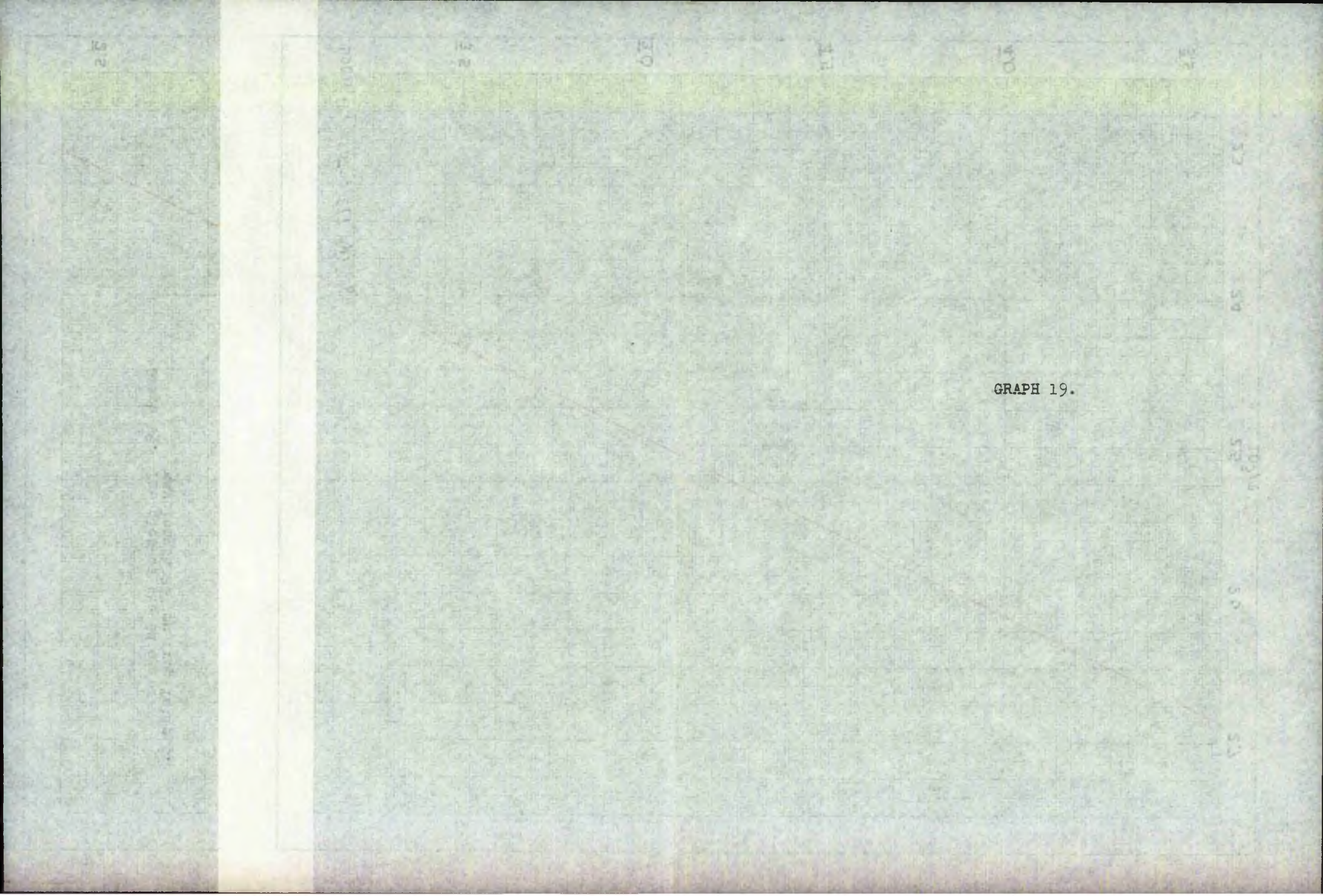
THE THERMAL DECOMPOSITION OF MERCURY DI-(p-CHLORBENZYL) IN ISO-OCTANE.

The experiments on the thermal decomposition of mercury di-(p-chlorbenzyl) dissolved in iso-octane were carried out under vacuum conditions in a manner analogous to those described for mercury dibenzyl. The analyses were also carried out in a similar manner to those described for mercury dibenzyl.

In this case, however, it was found that the ultra-violet absorption of the product, which at this stage was assumed to be p,p'-dichlordibenzyl, showed maxima which were shifted to longer wavelengths than those for the dibenzyl, and were somewhat intensified. Graphs 17 and 14 compare these product spectra. Thus, in order to obtain consistent first-order plots of $\log_{10}$(optical density) against time, it was essential to correct the O.D. readings at all wavelengths for product absorption, as described on page 64. The results for a typical experiment, corrected for product absorption, are indicated in Graph 18. Appendix 2 illustrates the full data for this experiment, and shows the reproducibility which was attained.

The data for all the experiments with mercury di-(p-chlorbenzyl).

The first order velocity constants, determined from the graphs of $\log_{10}$(corrected O.D. of the solutions at wavelengths 272 mμ or 277 mμ or 285 mμ) plotted against time , for the decomposition of mercury di-(p-chlorbenzyl) in iso-octane in the absence of air are given in Table 8.



GRAPH 19.

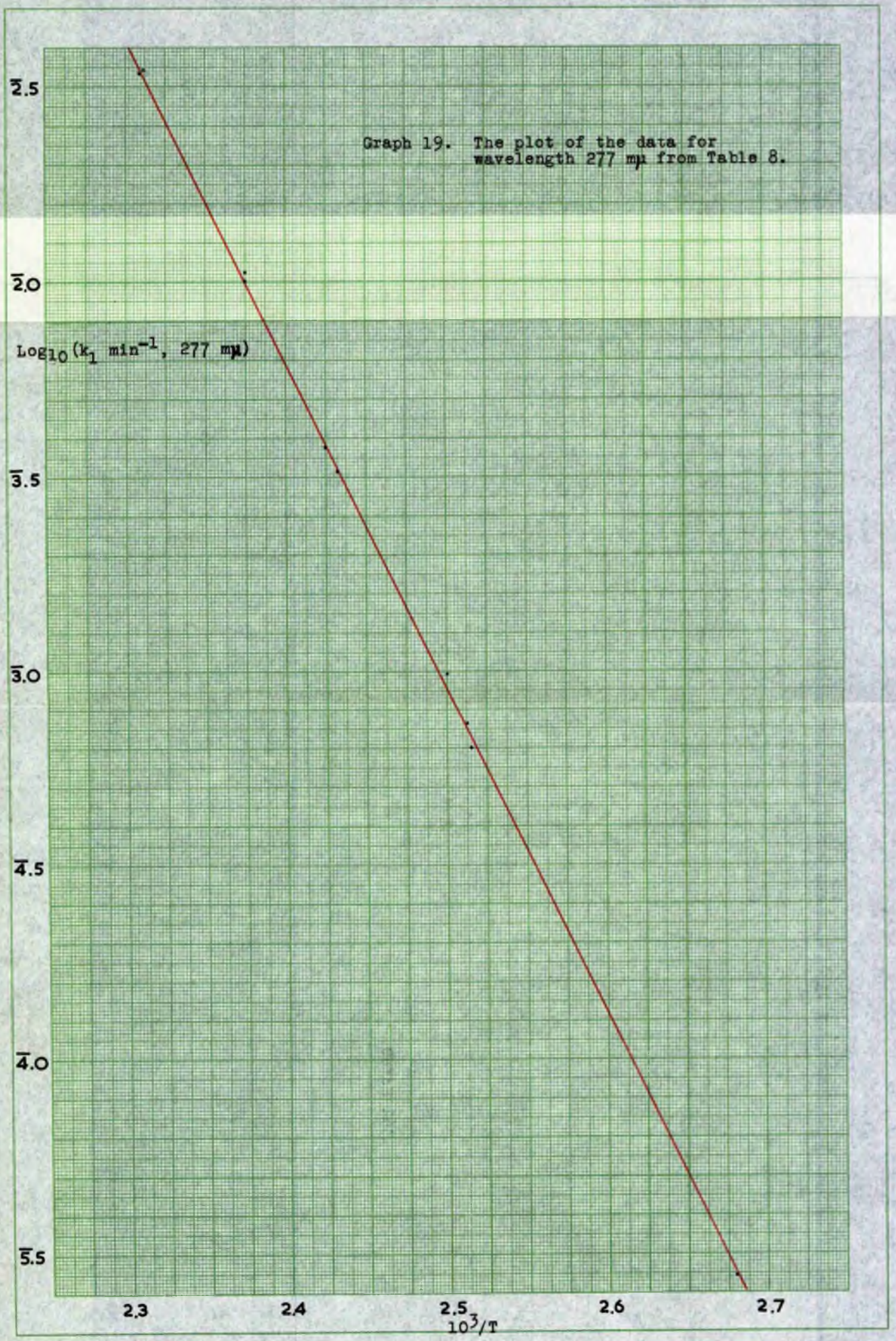

Graph 19. The plot of the data for wavelength 277 mμ from Table 8.
$\bar{2}.5$
$\bar{2}.0$
$\bar{3}.5$
$\bar{3}.0$
$\bar{4}.5$
$\bar{4}.0$
$\bar{5}.5$
$\text{Log}_{10}(k_1\ \text{min}^{-1},\ 277\ \text{m}\mu)$
2.3
2.4
2.5
2.6
2.7
$10^3/T$

Table 8. Data for Experiments with Mercury Di-(p-chlorbenzyl).

Expt. No.	°C.	°T.	$10^4/T$	$\log_{10}k_1$ 272 mμ min^{-1}	$\log_{10}k_1$ 277 mμ min^{-1}	$\log_{10}k_1$ 285 mμ min^{-1}	Approx. final % decomp.
31/I	139.1	412.3	24.25	-	$\bar{3}.580$	$\bar{3}.583$	75
33/I	160.0	433.2	23.08	-	$\bar{2}.531$	$\bar{2}.531$	75
34/I	159.5	432.7	23.11	$\bar{2}.542$	$\bar{2}.539$	$\bar{2}.540$	74
35/I	148.2	421.4	23.73	$\bar{2}.022$	$\bar{2}.024$	$\bar{2}.020$	85
36/I	148.2	421.4	23.73	$\bar{2}.015$	$\bar{2}.004$	$\bar{2}.002$	86
37/I	138.0	411.2	24.32	$\bar{3}.521$	$\bar{3}.517$	$\bar{3}.509$	77
38/I	126.7	399.9	25.00	$\bar{3}.015$	$\bar{4}.992$	$\bar{4}.964$	47
39/I	124.9	398.1	25.12	$\bar{4}.871$	$\bar{4}.864$	$\bar{4}.899$	71
40/I	124.4	397.6	25.15	$\bar{4}.797$	$\bar{4}.800$	$\bar{4}.802$	76
41/I	100.0	373.2	26.80	$\bar{5}.438$	$\bar{5}.445$	$\bar{5}.445$	62

The sparing solubility of the mercury di-(p-chlorbenzy) in iso-octane at room temperature restricted the investigation of this decomposition using the techniques already described to the concentration range 3.08×10^{-4} moles/l. to 1.86×10^{-4} moles/l.

Graph 19 shows $\log_{10}k_1$ plotted against $10^3/T$, using the data at wavelength 277 mμ from Table 8.

The variation of the first order velocity constant with temperature was found to follow the equation

$$k_1 = 10^{16.00}.\exp(-38,100/RT) \text{ sec.}^{-1}$$

by using the method of least squares (41) to fit the best straight line to the average of the $\log_{10}k_1$ data at wavelengths

272 mμ, 277 mμ and 285 mμ for each of the Experiments in Table 8.

THE INVESTIGATION OF THE THERMAL DECOMPOSITION OF MIXTURES OF MERCURY DIBENZYL AND MERCURY DI-(p-CHLORBENZYL) IN ISO-OCTANE.

The results for the individual decompositions of the mercury dibenzyl and the mercury di-(p-chlorbenzyl) indicated that these materials, when dissolved in iso-octane, decomposed at approximately equal rates at the same temperature. Thus condition (a) mentioned on page 77 was adequately fulfilled, and the decomposition of mixtures of these materials was next attempted.

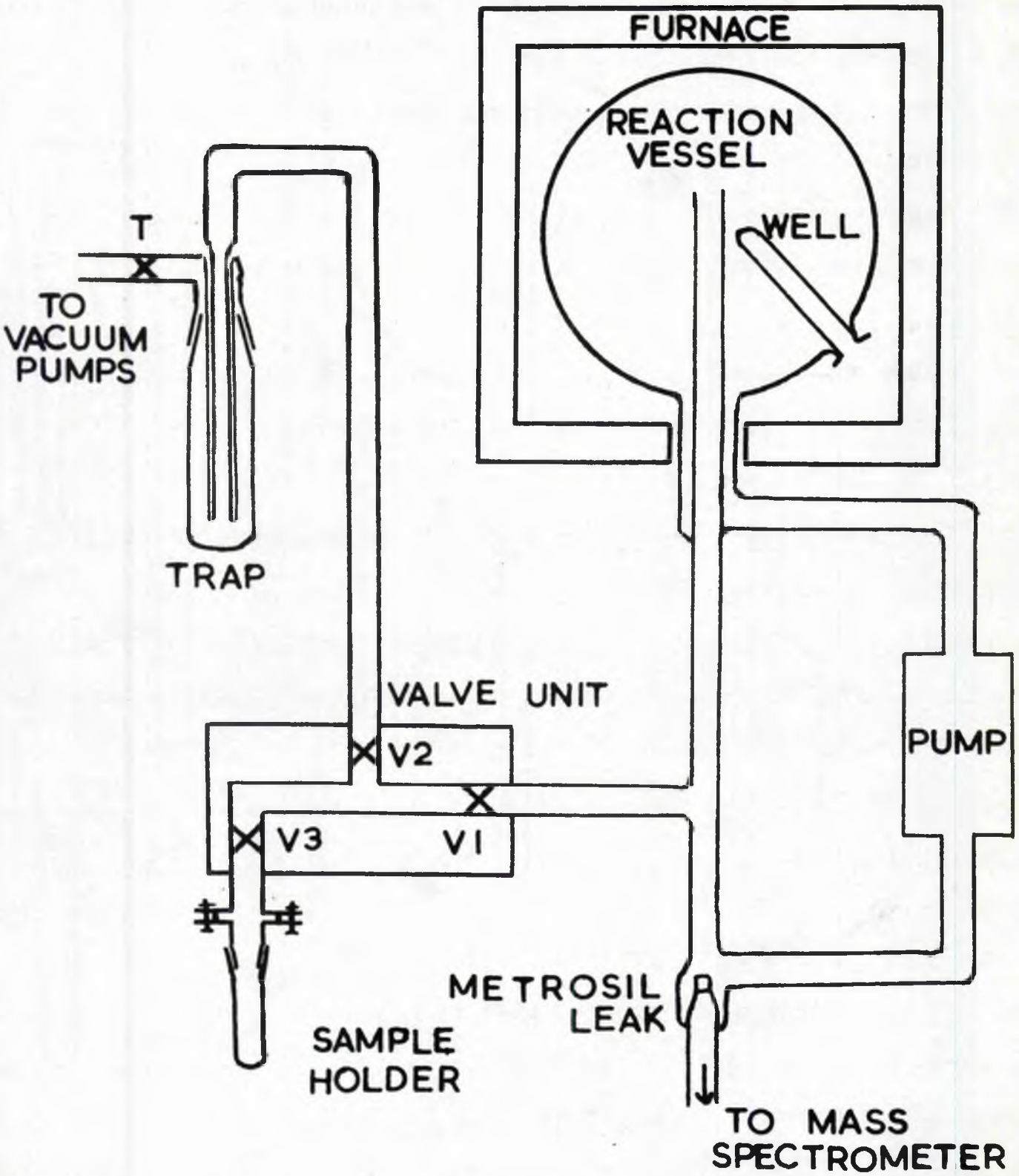
Because of the similarity of the ultra-violet absorption spectra of the dibenzyl and the p,p'-dichlordibenzyl, it was considered that some analytical technique other than u-v absorption spectroscopy would be needed to detect the expected cross-product, p-chlordibenzyl, in the presence of the other two materials. It seemed that the second mass spectrometer which was available in the Department would provide a suitable analytical tool for this problem, and satisfy the requirements of condition (d) mentioned on page 78.

The use of the mass spectrometer capable of analysing solids.

The original capabilities of this instrument, designed originally for the analyses of gases of low molecular weight and partially built by Mr. W. F. Volume, B.Sc., had been considerably extended by Mr. R.N. Pittilo, B.Sc., who designed a valve injection unit for handling relatively volatile solids of the dibenzyl type, and by Mr. I.M.T. Davidson, B.Sc., who

FIGURE 23.

Fig. 23.



A diagram of the system used to inject volatile materials into the mass spectrometer.

rebuilt the ion-gun and ion collector assemblies to enable work requiring resolution up to 1 part in 200 atomic mass units to be performed, and who also constructed a furnace for a 2 litre reaction vessel which was directly attached to the mass spectrometer (58), (59).

Figure 23 shows the system which was used to inject the vapour from volatile solids into the mass spectrometer. The operation of this system was as follows :-

When not in use, the whole apparatus up to tap T was kept evacuated, because the system was permanently open to the mass spectrometer via the metrosil leak. When required for an analysis, the furnace was heated to the temperature desired, and maintained at that value by subsidiary heaters operated from a control unit which was sensitive to changes in the resistance of a platinium resistance thermometer inserted near the reaction vessel. A thermocouple inserted in the well indicated the temperature attained. The glass lines, the inlet line to the mass spectrometer beyond the leak, the pump, the valve unit and the sample holder were also heated, usually to a temperature slightly lower than that of the reaction vessel.

The temperatures of the various parts of the system had to be carefully selected experimentally to be high enough to prevent condensation of the material under analysis, yet not so high as to cause decomposition of the material. During other applications of this system (59), the temperature of the reaction vessel was sufficiently high to cause the slow decomposition or interaction

of materials injected for kinetic studies.

Before the injection of a material, the whole apparatus was pumped to remove traces of previously injected materials. With the valve V 2 shut, a background spectrum of the regions of interest was then obtained with the mass spectrometer.

With valves V 1, V 2 and V 3 shut, the sample holder was removed, cooled and charged with the material for analysis, and was then replaced.

The air in the sample holder was then removed by pumping with the valves V 2 and V 3 and the tap T open. (With volatile samples, the sample holder was cooled with liquid oxygen or solid carbon dioxide/acetone slush during the removal of the air). The valves and tap were then shut, and the sample holder was reheated to the temperature desired with an oil, water or air bath. Valves V 1 and V 3 were then opened and the vaporised solid was injected into the reaction vessel. Under suitable conditions, it was possible to volatilise all the solid placed in the sample holder. Valves V 1 and V 3 were then shut. (In certain instances, difficulties arose if the solid injected was a mixture with components of widely differing volatilities. In such cases, the operation of the pump unit sometimes assisted the entry of the less volatile materials).

A spectrum obtained immediately after the injection of a sample usually showed very small peaks. These grew slowly until ultimately maximum intensities were attained. The effect was attributed to adsorption of the injected materials onto the

long inlet line between the leak and the ionisation chamber of the mass spectrometer; the slow decay in the intensities of the peaks observed after all materials had been removed from the system to the cooled trap after an analysis was probably related to the slow desorption of the materials from these areas of the mass spectrometer. The system had to be modified at a later date to enable accurate quantitative analyses to be performed on these readily adsorbed materials - the leak was moved to a position immediately over the ionisation chamber of the mass spectrometer. Unfortunately, this modification could not be carried out before the work reported below had been completed, thus only qualitative analyses were possible on the products obtained from the decompositions of mixtures of mercury dibenzyl and mercury di-(p-chlorbenzyl).

The initial investigations of the products formed from the decomposition of mixtures of mercury dibenzyl and mercury di-(p-chlorbenzyl), dissolved in iso-octane.

Some initial decompositions were performed with both the pure components separately and with mixtures which produced mercury sufficient to perform gravimetric analyses similar to those reported for mercury dibenzyl on page 34.

Quantities of the solid reactants were weighed directly into the clean reaction vessels, 1.02 ml. of spectroscopic grade iso-octane solvent was added to each vessel, and the liquids were then degassed four times. The vessels were then sealed.

The reactions were carried out at 140°C. for 72 hours. The appearances of the products in the vessels at the end of this period are noted in the Table below.

Vessel No.	gm. mercury dibenzyl	gm. mercury di-(p-chlorbenzyl)	Appearance of product
1	0.1036	0.1142	Hg only + solution
2	0.1360	0.1458	Hg only + solution
3	-	0.1395	(considerable ppt.+
4	-	0.1433	(Hg + solution
5	0.1866	-	Hg only + solution

Thus, it was immediately obvious from a visual inspection of these reaction vessels that some additional changes had occurred in the mixed reactions which had yielded a more soluble product.

The analysis of the products from vessels 2 and 3.

Approximately 0.1 ml. of the solution was removed from the vessel No. 2 after the reaction. This solution was placed in a small tared combustion tube and the solvent was evaporated. 7.1 mgm. of solid was obtained. An analysis of this solid was attempted with the mass spectrometer adapted for the analysis of solids.

No conclusive evidence for the presence of any material other than dibenzyl was obtained from this initial experiment. It was thus suspected that the other products were less volatile than the dibenzyl, and the failure to observe any other material could have been caused by too low a temperature in the bath which surrounded the sample holder.

The experiment was repeated, using the remainder of the

TABLE 9.

Table 9.

Summary of the observations made during the analyses of vessels 2 and 3.

Material	M.W.$^{\phi}$	Peaks in the m/e region 175-185	215-220	245-255
pure dibenzyl	182	present"	-	-
pure p,p'-dichlordibenzyl (vessel 3, sample holder at 135°C.)	250	present	-	present
products of the mixed reaction (vessel 2, sample holder at 100°C.)	182 216 250	present	present	-†

ϕ M.W. of the most abundant molecular species.

" Known from previous work with dibenzyl and this mass spectrometer. Subsequently proved with a sample of dibenzyl prepared from the decomposition of mercury dibenzyl. (See also ( )).

† The absence of peaks in this region is now known to have been due to too low a temperature round the sample holder, and the relative involatility of the p,p'-dichlordibenzyl. During subsequent work at higher temperatures, definite peaks were found in this region from products of mixed reactions. (See e.g. Fig. 24).

solution from vessel 2. With the sample holder at a temperature of 100°C. and the valve unit at 140°C., peaks were obtained in in the mass spectrum in the mass/charge (m/e) regions 178-183 (peak height 84.5 mV.) and 215-220 (31.5 mV.). No peaks could be detected in the m/e 245-255 region. (Note. The molecular weights of the parent molecules expected as products are :- dibenzyl 182.3, p-chlordibenzyl 216.7 and p,p'-dichlordibenzyl 251.1 . These are, of course, the mean molecular weights of these materials. The mass spectra will display the isotopic constitution of the molecules due to the carbon and chlorine isotopes. The characteristic mass spectrum of dibenzyl in the m/e 178-183 region was already well known from other work).

A subsequent analysis of pure p,p'-dichlordibenzyl, obtained from vessel 3, with the sample holder at 135°C. showed considerable peaks at m/e 175-185 (48 mV.) and at m/e 245-255 (13 mV.), and no peaks in the m/e 215-220 region.

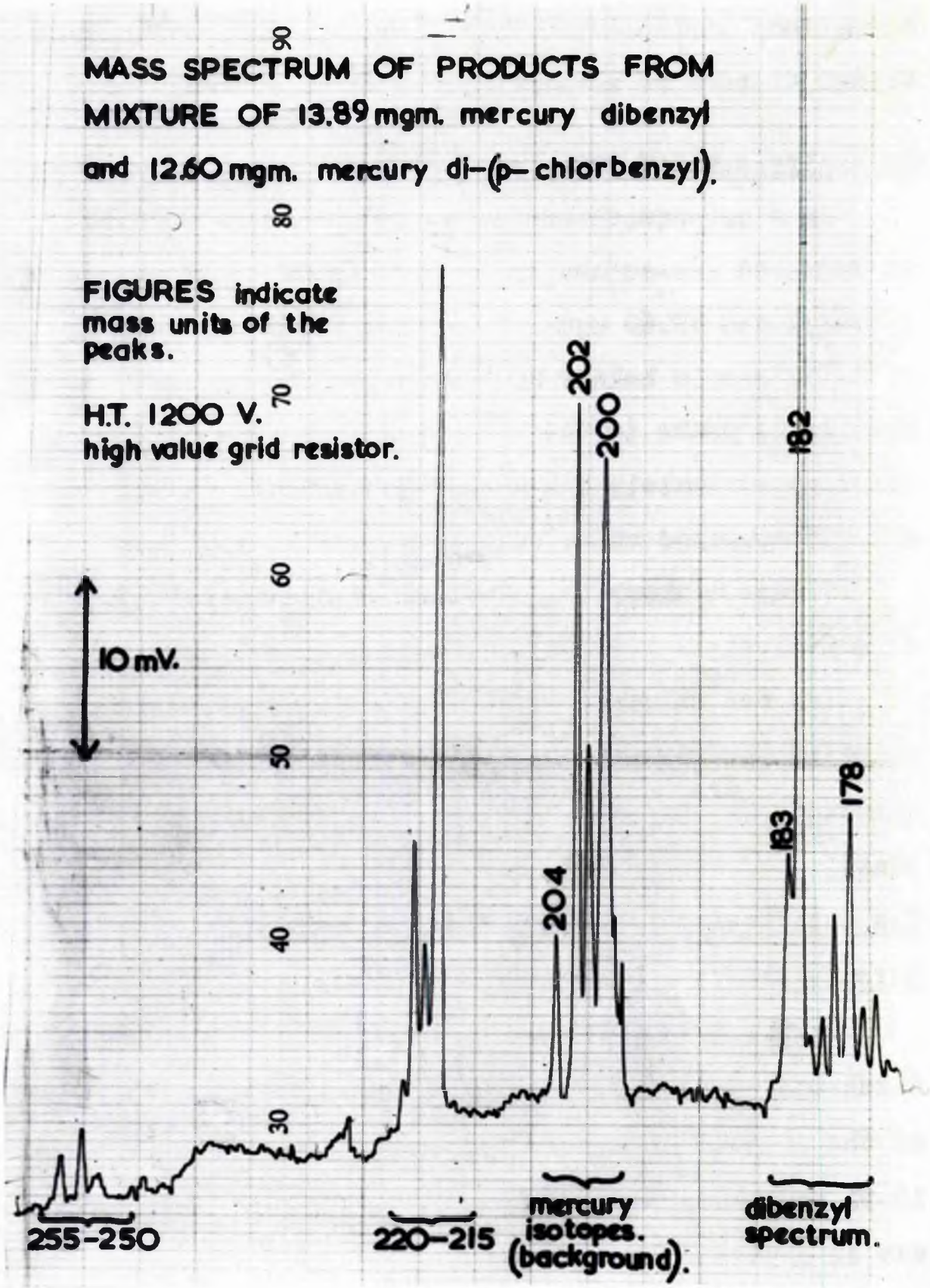
These observations are summarised in Table 9.

Thus, the presence of peaks in the region m/e 215-220 from the products of the mixed reaction in vessel 2, which were absent from the mass spectrum of the product from the decomposition of the mercury di-(p-chlorbenzyl) in vessel 3 may be taken as preliminary evidence for the production of p-chlordibenzyl in the mixed reaction.

These experiments were repeated under more favourable analytical conditions, and comparison spectra were obtained from authentic samples of dibenzyl, p-chlordibenzyl and

FIGURE 24.

Fig. 24.


MASS SPECTRUM OF PRODUCTS FROM MIXTURE OF 13.89 mgm. mercury dibenzyl and 12.60 mgm. mercury di-(p-chlorbenzyl).
FIGURES indicate mass units of the peaks.
H.T. 1200 V. high value grid resistor.
10 mV.
90
80
70
60
50
40
30
202
200
182
204
183
178
255-250
220-215
mercury isotopes. (background).
dibenzyl spectrum.

p,p'-dichlordibenzyl prepared by other chemical methods. These additional observations confirmed the conclusions quoted above. Copies of some of the spectra obtained are given below.

An analysis under more favourable analytical conditions.

In a subsequent analysis, the products from the decomposition, in degassed iso-octane, of a mixture of 13.89 mgm. of mercury dibenzyl and 12.60 mgm. of mercury di-(p-chlorbenzyl) injected from the sample holder at 160°C. yielded initially a spectrum displaying peaks in the m/e 175-185 and 215-220 regions. After approximately 2 hours, several peaks in the m/e region 245-255 appeared and slowly increased in magnitude.

Figure 24 shows the spectrum obtained at this stage during this analysis.

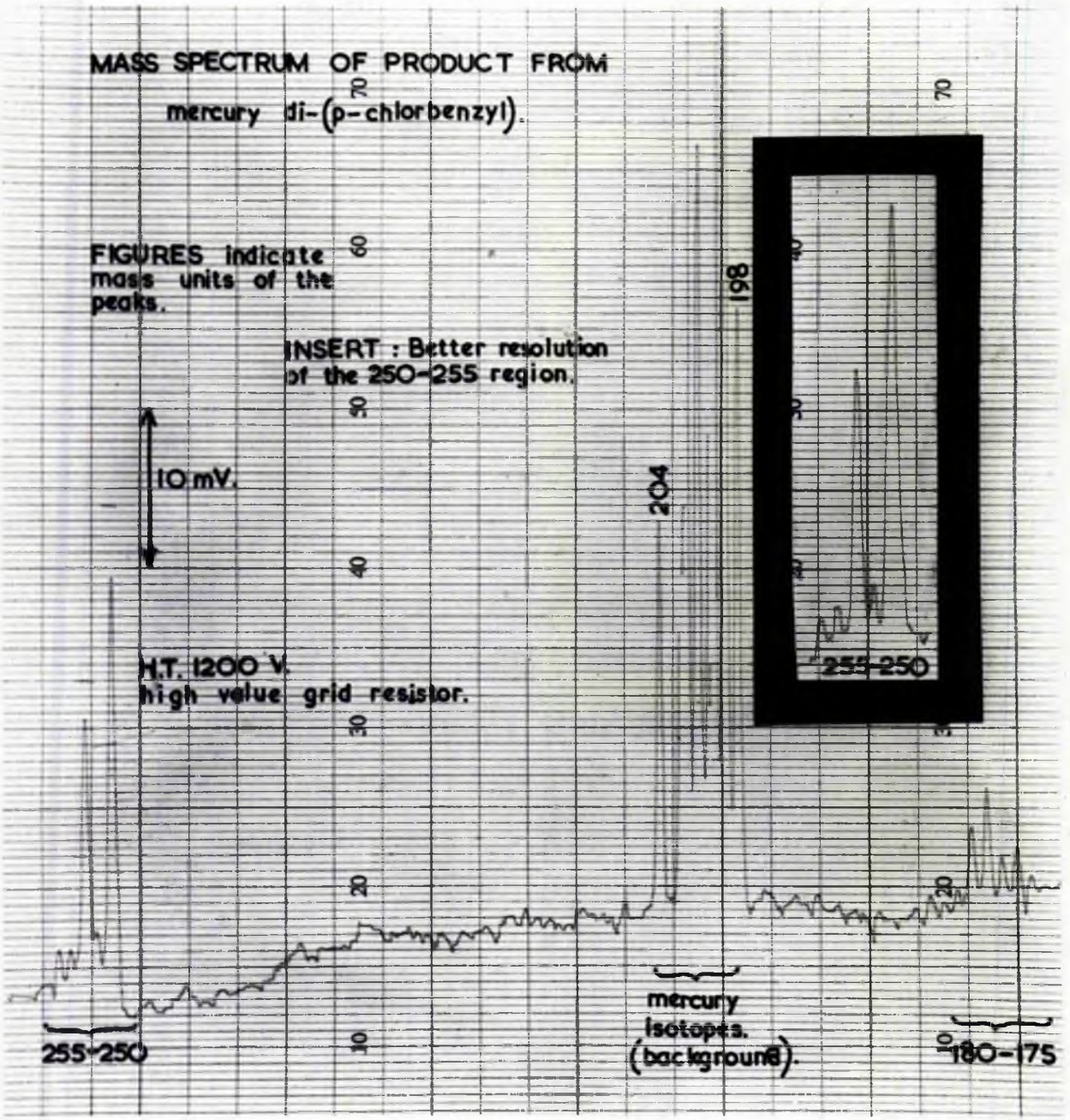
(As far as possible, the mercury produced during this reaction was not transferred to the sample holder - it was necessary to construct certain parts of the valve unit from brass).

The mass spectrum of the product from the decomposition of mercury di-(p-chlorbenzyl).

Figure 25 shows a spectrum over the m/e region 170-255 which was started 1 hour and 20 minutes after the injection of the product obtained from the total decomposition of 15.91 mgm. of pure mercury di-(p-chlorbenzyl) in the absence of air in degassed iso-octane. The peaks in the m/e region 250-255 were obtained 1 hour and 52 minutes after the injection

FIGURE 25.

Fig. 25.


MASS SPECTRUM OF PRODUCT FROM
mercury di-(p-chlorbenzyl).
FIGURES indicate mass units of the peaks.
INSERT : Better resolution of the 250-255 region.
10 mV.
H.T. 1200 V.
high value grid resistor.
204
198
255-250
mercury isotopes. (background).
180-175
255-250

of the sample, by which time these peaks had almost attained their maximum intensity. (The instrument background over the same region, obtained immediately before the injection of this sample, displayed only the mercury isotopes).

After this spectrum had been obtained, pure dibenzyl was injected into the system without removing the previous sample (Valve V 1, Fig. 23 was shut during the manipulation of the sample holder, and reopened to admit the second sample) and a spectrum of the mixture of these two materials was obtained. No peaks in the mass region 215-220 were produced from this mixture when the furnace was at its usual operating temperature of approximately 280°C., even after an hour and 10 minutes.

Thus, it was conclusively proved that the peaks in the m/e region 215-220 did not arise from the product of the decomposition of the mercury di-(p-chlorbenzyl), shown below to be p,p'-dichlordibenzyl, or from this product when pure dibenzyl was added when the furnace was held at 280°C.; i.e. the cross-product observed from the mixed reactions could not have been formed during the mass spectrometric analyses from the dibenzyl and p,p'-dichlordibenzyl present in the analytical instrument.

The origin of the cross product.

There remained the possibility that the cross product had been formed by the interaction of the dibenzyl and the p,p'-dichlordibenzyl which were produced during the mixed thermal decompositions of the two mercury compounds in iso-octane.

Two reaction vessels containing mixtures of dibenzyl and p,p'-dichlordibenzyl were sealed under vacuum conditions with degassed iso-octane and were kept at 157.5°C. for 13 hours and 10 minutes. Analyses of the residual materials by the mass spectrometer showed that the material which gave the peaks in the m/e region 215-220 in the previous spectra had not been formed.

Thus, it was concluded that the material which yielded the peaks in the mass region 215-220 had been formed directly from the mixture of the mercury dibenzyl and the mercury di-(p-chlorbenzyl) or from their initial decomposition products. In view of the fact that the decomposition of these two mercury compounds proceeds according to the first order law, the latter mode of formation is the more probable. (See page 77).

<u>The identity of the product from the thermal decomposition of mercury di-(p-chlorbenzyl).</u>

The reasons for believing that the product from the thermal decomposition of mercury di-(p-chlorbenzyl) was p,p'-dichlordibenzyl can be listed as below.

(i) By analogy with the decomposition of mercury dibenzyl which gave dibenzyl, p,p'-dichlordibenzyl was to be anticipated from mercury di-(p-chlorbenzyl).

(ii) The ultra-violet spectrum of the product, Graph 17, resembled closely the known spectrum of dibenzyl, except that the peaks in the product spectrum were moved approximately 10 mμ to longer wavelengths, and the twin peaks at 264.5 mμ and

TABLE 10.

Table 10.

The Distribution of Isotopic Molecules of p,p'-dichlordibenzyl.

M.W.[ø]	Theoretical distribution	Theoretical peak height ratio[x]	Observed peak height ratio[→] (Insert, Fig. 25)	
(M + 70)	100%	100%	65mm.	100%
(M + 72)	65.2%	65.2%	42mm.	64.6%
(M + 74)	10.6%	10.6%	6mm.	9.2%

ø M is taken as the M.W. of the molecular skeleton, which is assumed to be formed from mono-isotopic elements, i.e. the smaller carbon isotope peaks at (M'+ 70), (M"+ 72) and (M"'+ 74) have been omitted from this Table.

x Assumes equal instrumental sensitivity for all the isotopic molecules.

→ The assignment of a particular mass number to a specific peak was attempted by refocussing the mass spectrometer from the known mercury isotope peaks to the peaks in the mass region 245-255 units, by making measured adjustments to the drawout voltage of the ion gun of the mass spectrometer. On simple theory, the plot of mass collected against corresponding drawout voltage should be linear. A non-linear relationship was found for this instrument, thus making mass number allocations more difficult. In the instances quoted in this Table it was assumed that the largest peak was formed as the parent ion from the most abundant molecular species.

268.5 mμ in the dibenzyl spectrum had become a single peak of enhanced intensity at 277 mμ.

(iii) Under suitable conditions the mass spectrum of the product indicated 5 peaks in the mass region 245-255 units. Theoretically, from the known chlorine isotope ratio of ^{35}Cl 75.4%, ^{37}Cl 24.6%, a material which contained 2 chlorine atoms per molecule should show the molecular weight distribution indicated in Table 10. This should be related to the peak-height ratio of the peaks corresponding to these masses in the mass spectrum of the compound, as shown. The ratios of the peak-heights as observed are also indicated.

It is known that dibenzyl (M.W. 182) produces a small isotopic peak at m/e 183, together with a considerable parent ion peak at m/e 182 (60).

Thus, it would be expected that p,p'-dichlordibenzyl would produce 3 main parent ion peaks, separated by 2 mass units, corresponding to the chlorine isotope distribution, each with a small satellite peak at 1 mass unit greater corresponding to the dibenzyl carbon isotope peak.

Figure 25 shows 5 of these 6 predicted peaks, in a mass spectrum produced by the product under discussion.

(iv) A sample of the product was obtained, and it had a m.pt. 78-100°C. (uncorrected). A sublimate was observed, and it was collected. The m.pt. of the sublimed material was 99.75-100.25°C. (corrected). (The wide range of m.pt. of the unsublimed product is attributed to (1) the tenacious retention

TABLE 11.

Table 11. Melting points of p,p'-dichlordibenzyl.

M.pt.	112°C	111°C	112°C	
Method of preparation	chlorine on dibenzyl 0.7% iodine	aqua regia on dibenzyl	p-Cl toluene over glowing Pt wire	p-C + H sun
Method to prove p,p'-structure	oxidation to p-chlor-benzoic acid m.pt. 230°C.	-	-	
Other evidence	analyses for C, H and Cl correct	analysis for chlorine correct	analyses for C and H correct	mix cor
Reference	(61)	(62)	(63)	

M.pt.	100°C	99.75-100.25°C	99.25-100.0°C	95.
Method of preparation	p-Cl benzyl bromide + zinc	thermal decomposition of $(p\text{-ClBz})_2Hg$	p-Cl benzyl chloride + Mg + $CuCl_2$	p,p dib cat
Method to prove p,p'-structure	-	-	oxidation to p-chlor-benzoic acid	
Other evidence	analyses for C and H correct	M.W. correct. U.V. spectrum similar to Bz_2 spectrum	mixed m.pt. of acid correct. (N.M.R. study see Appendix 3)	U.V sim Bz_2
Reference	(65)	page 94.	page 110.	pag

of the solvent by the product, even when the solvent was removed by distillation under high vacuum, and (ii) the possible presence of mercury in the product).

In addition, the sublimation was performed under high vacuum conditions, and this gave a product of m.pt. 97.25-99.85°C. (corrected).

Five m.pts. for p,p'-dichlordibenzyl are available in the literature, and are shown in Table 11. Of these, only the most recent, observed by Fuson and Cooke, agrees with the value for the sublimed material quoted above. Because these authors did not report establishing a structure for their material, it was considered necessary to prepare p,p'-dichlordibenzyl by other methods, to establish its structure by oxidation or other methods and to determine the m.pt. of the materials obtained.

Two attempts to prepare this material are reported below, and the results have been added to those in Table 11.

The preparation of p,p'-dichlordibenzyl.

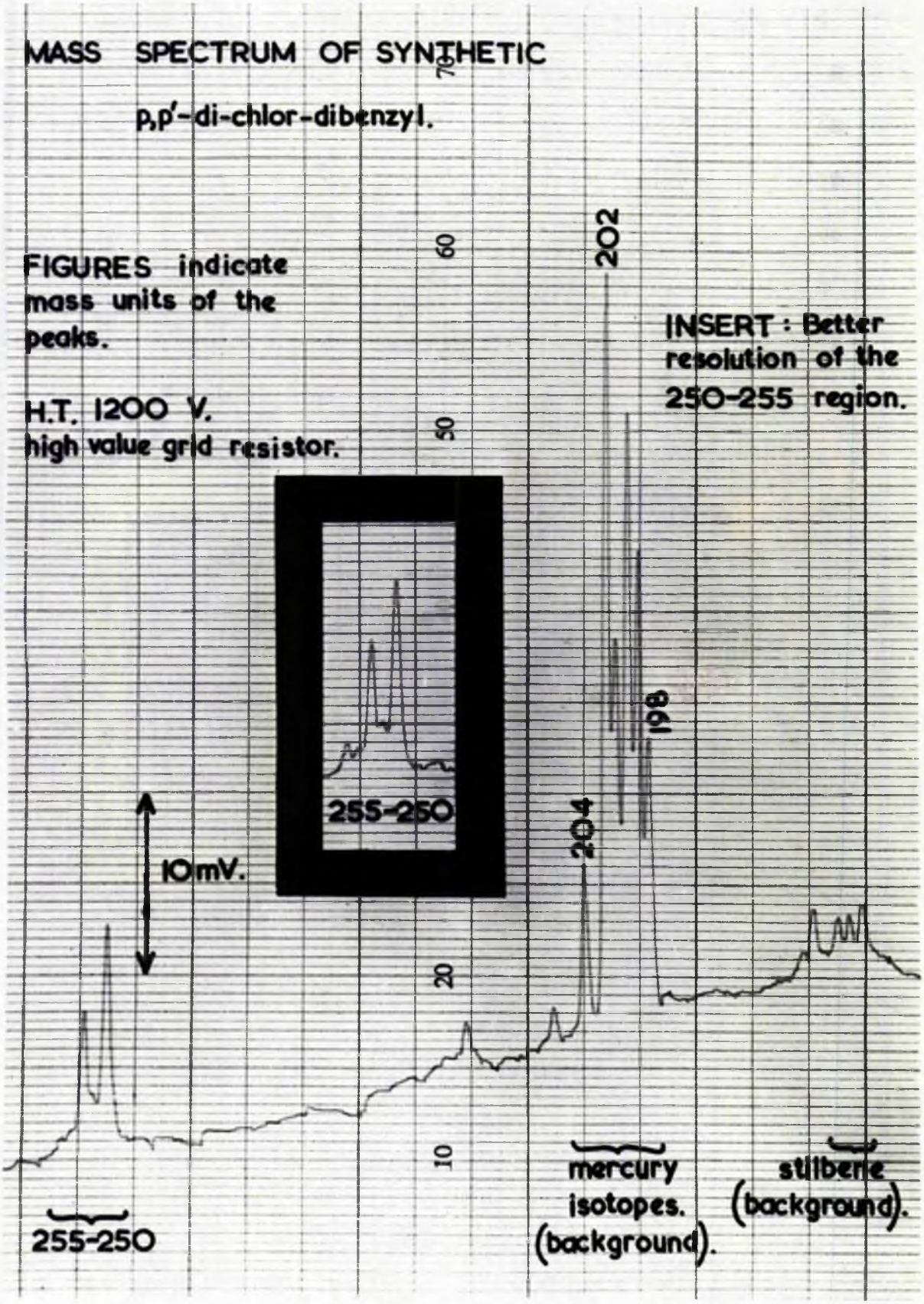
(i) From p-chlorbenzyl chloride.

Sodium-dried ether was boiled under reflux, then 2.41 gm. of magnesium was added. 15.8 gm. of p-chlorbenzyl chloride was added under continued reflux, and a green Grignard solution was formed. When anhydrous cupric chloride (1.41 gm.) was added, a vigorous reaction occurred and an intense purple colour developed. The refluxing was continued for 2 hours. (73).

The ether was distilled off, and water added cautiously to

FIGURE 26.

Fig. 26.


MASS SPECTRUM OF SYNTHETIC
p,p'-di-chlor-dibenzyl.
FIGURES indicate mass units of the peaks.
H.T. 1200 V.
high value grid resistor.
INSERT : Better resolution of the 250-255 region.
70
60
50
20
10
202
198
204
255-250
10mV.
255-250
mercury isotopes. (background).
stilbene (background).

the solid residue until no further reaction occurred. A slight excess of concentrated hydrochloric acid was added, and the mixture filtered. The residue was extracted with 30 ml. of a methanol/chloroform mixture. This extract was treated twice with decolourising charcoal. Evaporation of the colourless solution gave white needle crystals, a sample of which sublimed when a melting point determination was attempted. The crude product was therefore sublimed under high vacuum conditions, and gave a material of m.pt. 95.3-99.9°C. (corrected). (The majority of the crystals melted between 98.25 and 99.9°C.). A small sample of the sublimed material was re-sublimed at 95°C. in air, and the m.pt. was sharpened to 99.25-100.0°C. (corrected). A sample of this re-sublimed material gave the ultra-violet spectrum shown in Graph 17.

A mass spectrum of the sublimed material gave indications of peaks in the m/e region 255-250, of similar relative intensities to those obtained with the product from the thermal decomposition of the mercury di-(p-chlorbenzyl), thus indicating a material of similar molecular weight. Figures 25 and 26 compare these mass spectra.

From the similarity of the ultra-violet spectra, the m.pts. and the mass spectra for the thermally produced and the synthesised materials, it was concluded that they had identical molecular structures.

<u>The oxidation of the synthetic material</u>.

Trial oxidations of the material with potassium dichromate

and concentrated sulphuric acid gave an acidic product, small quantities of which sublimed very readily in air before melting.

Authentic samples of p-chlorbenzoic acid (literature m.pt. 236°C), the expected oxidation product, also sublimed very readily in air at temperatures above 180°C.

A mixture of 1 ml. of water, 3 ml. of glacial acetic acid and 1 ml. of concentrated sulphuric acid was added to 0.3319 gm. of the compound, the liquid was heated to reflux temperature, and 0.8584 gm. potassium dichromate (an excess) was added in small portions during ½ hour. A solid separated out during the oxidation. After 1 hour, the reaction mixture was cooled and diluted with 75 ml. of distilled water, and the precipitate was filtered off. The residue was treated with 50 ml. of warm 2 N. sodium hydroxide, and the mixture was refiltered. There remained 0.1072 gm. of a yellow crystalline material.

The alkaline filtrate was acidified with hydrochloric acid, and the copious white precipitate was filtered off, dried and weighed (0.2526 gm.). The m.pt. of this acidic material, sealed in a capillary tube, was 237-241.8°C. (uncorrected). The m.pt. of an authentic sample of p-chlorbenzoic acid under similar conditions was 240.0-242.5°C. (uncorrected). A mixture of these two materials melted, under similar conditions, at 238.0-243.0°C. (uncorrected). The oxidation product was thus identified as p-chlorbenzoic acid.

The yield of p-chlorbenzoic acid was 61% of the theoretical

amount from 0.3319 gm. of p,p'-dichlordibenzyl.

The yellow compound indicated above was obtained in larger yields during other oxidations with the theoretical quantities of potassium dichromate, and it was identified as p,p'-dichlorbenzil by the m.pt. for a sublimed sample, 195.5-197.5°C. (corrected). (Literature m.pts. 195-196°C. (66), 193°C. (67), 191°C. (67), 200°C. (68)). An attempt was made to convert some of the p,p'-dichlorbenzil to the mono-phenyl hydrazone. Tiny yellow needle crystals were obtained. These were recrystallised from ethyl alcohol and dried. The m.pt. of this derivative was 172.6-181.2°C. (corrected). The literature m.pt. for the mono-phenyl hydrazone is 178°C. (67).

If it is assumed that all of the 0.1072 gm. of the yellow material obtained during this oxidation is p,p'-dichlorbenzil, then the yield of the p-chlorbenzoic acid from the p,p'-dichlordibenzyl remaining is 86%.

The high yield of p-chlorbenzoic acid during this oxidation, together with the isolation of the intermediate p,p'-dichlorbenzil, made it possible to conclude that the material of m.pt. 99.25-100.0°C. (corrected) was the p,p'-dichlordibenzyl which was required.

The preparation of p,p'-dichlordibenzyl.

(ii) From p,p'-dinitrodibenzyl.

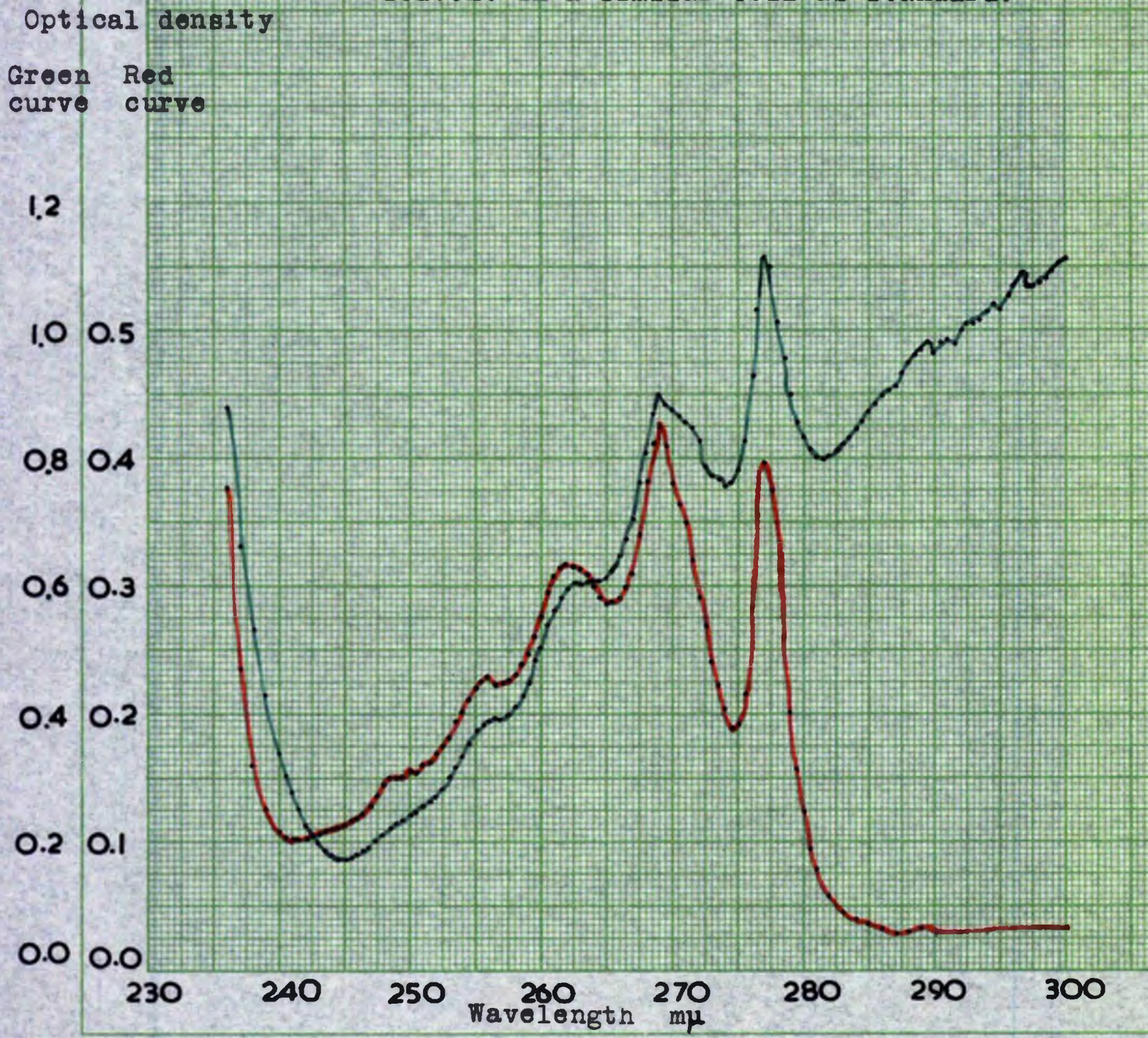
p,p'-dinitrodibenzyl, of m.pt. 180.75-182.0°C. (corrected) (literature m.pt. 179-180°C.), prepared by the air oxidation of p-nitrotoluene dissolved in alcoholic potash solution (69),

Graph 20. Spectra of p,p'-dichlordibenzyl prepared from p,p'-dinitrodibenzyl.

Green curve. 0.865 mgm. compound, m.pt. 99.25-103.0°C., dissolved in 1.11 ml. iso-octane.

Red curve. 0.620 mgm. of catalytically hydrogenated material, of m.pt. 95.5-98.25°C., dissolved in 1.18 ml. of iso-octane.

The spectra were observed using a silica cell of 0.2 cm. optical path, against solvent in a similar cell as standard.



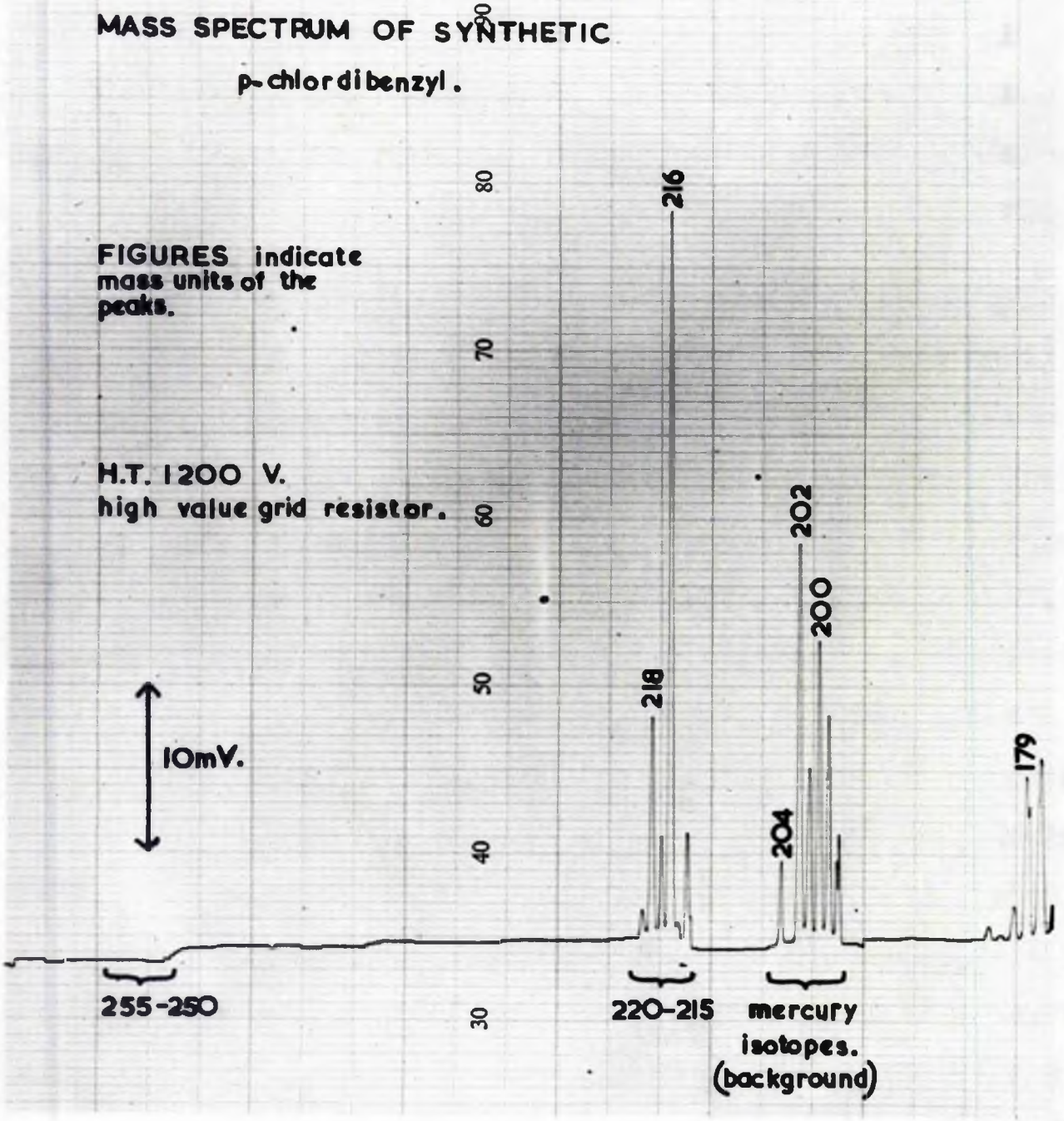
was catalytically reduced to p,p'-diaminodibenzyl with Raney nickel and hydrogen at 1 atmosphere pressure (70). The free diamine was somewhat unstable to air, and it was therefore converted to the di-hydrochloride. This salt (1 gm.) was diazotised and was then treated with cuprous chloride dissolved in concentrated hydrochloric acid. The reaction was completed by warming the mixture on a water bath. A red oil was obtained, which solidified when cooled to room temperature. The red solid was extracted with ethyl alcohol, and the solvent was distilled from the brown solution. The brown oily mass thus obtained contained some needle shaped crystals. A pale yellow crystalline material was obtained when this brown oil was sublimed at 90°C. in air. This sublimate was recrystallised twice from methyl alcohol, and white crystals of m.pt. 99.25-103.0°C. (corrected) were obtained. The ultra-violet absorption spectrum of this material, Graph 20, indicated the presence of some stilbene-type material. The product was therefore catalytically hydrogenated with palladium charcoal, and then recrystallised from methyl alcohol. The reduced material had a m.pt. of 95.5-98.25°C. (corrected), and an ultra-violet spectrum which corresponded closely to that of the material produced during the thermal decomposition of the mercury di-(p-chlorbenzyl). Graph 17 compares these spectra.

From all the evidence presented above, it can be concluded that the products of the thermal decompositions of mercury di-(p-chlorbenzyl) in degassed iso-octane were mercury, which

could be recovered in 98.9% yield, and p,p'-dichlordibenzyl of m.pt. 99.75-100.25°C. (corrected). Analyses of the spectral data indicated that the organic product was obtained in 121% yield. This high yield of product was attributed to the presence of a small quantity of a strongly absorbing material with the relatively weakly absorbing p,p'-dichlordibenzyl. In this instance, it was not possible to identify the impurity from an examination of the spectrum obtained (Graph 17).

FIGURE 27.

Fig. 27.


MASS SPECTRUM OF SYNTHETIC
p-chlordibenzyl.
FIGURES indicate mass units of the peaks.
H.T. 1200 V.
high value grid resistor.
10mV.
80
70
60
50
40
30
216
218
202
200
204
179
255-250
220-215
mercury isotopes. (background)

The identity of the cross product from the mixed decompositions.

The material from the mixed decompositions of mercury dibenzyl with mercury di-(p-chlorbenzyl) which yielded the mass spectra displaying peaks in the mass region 215-220 units (see Fig. 24) was suspected to be p-chlordibenzyl. This suspicion was confirmed by an independant synthesis of this material and the determination of its mass spectrum and its ultra-violet absorption spectrum.

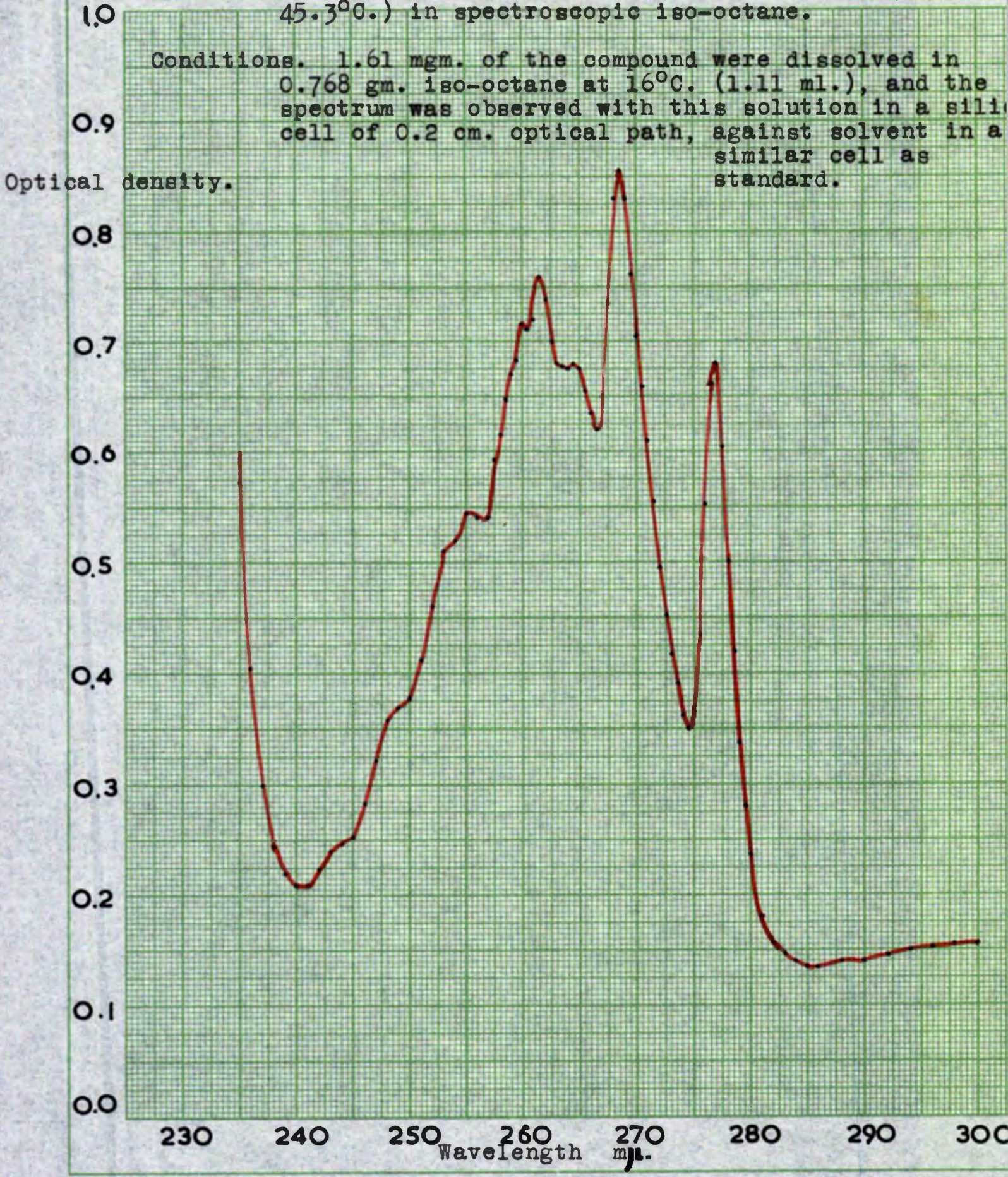
The preparation and properties of p-chlordibenzyl.

A sample of p-chlorstilbene was made by a Meerwein type reaction between diazotised p-chloraniline and cinnamic acid, according to the method given by Bergmann, Weizman and Schapiro (71). The product, when recrystallised twice from iso-propyl alcohol, melted at 126.0-129.4°C. (corrected). Literature m.pt. 129°C. (uncorrected), (71). This product was shown not to have been unchanged cinnamic acid by mixed melting point determination with a sample of the acid. (M.pt. of cinnamic acid 128.9-133.2°C. (corrected), mixed m.pt. of the acid with the product 103.0-127.0°C. (corrected)).

0.9138 gm. of this p-chlorstilbene, when reduced with hydrogen in the presence of Raney nickel, absorbed 109 ml. of the gas, measured wet at 17.5°C. and 76.3 cm. mercury pressure. The theoretical hydrogen uptake under these conditions was 103 ml. The ethyl alcohol, which was used as a solvent during this hydrogenation, was distilled off after the solution had been filtered to remove the catalyst. A white solid was

Graph 21. The spectrum of p-chlordibenzyl (of m.pt. 44.8-45.3°C.) in spectroscopic iso-octane.

Conditions. 1.61 mgm. of the compound were dissolved in 0.768 gm. iso-octane at 16°C. (1.11 ml.), and the spectrum was observed with this solution in a silica cell of 0.2 cm. optical path, against solvent in a similar cell as standard.



obtained which melted over the range 49.5-64.75°C. (corrected). The literature m.pt. for p-chlordibenzyl is 49°C. (uncorrected), (71).

The mass spectrum of the p-chlordibenzyl, shown in Fig. 27, indicated peaks in the mass region 215-220 units, as was expected from the previous work described above, but in addition there was a small peak just below this mass region which was attributed to the presence of a small quantity of unreduced p-chlorstilbene.

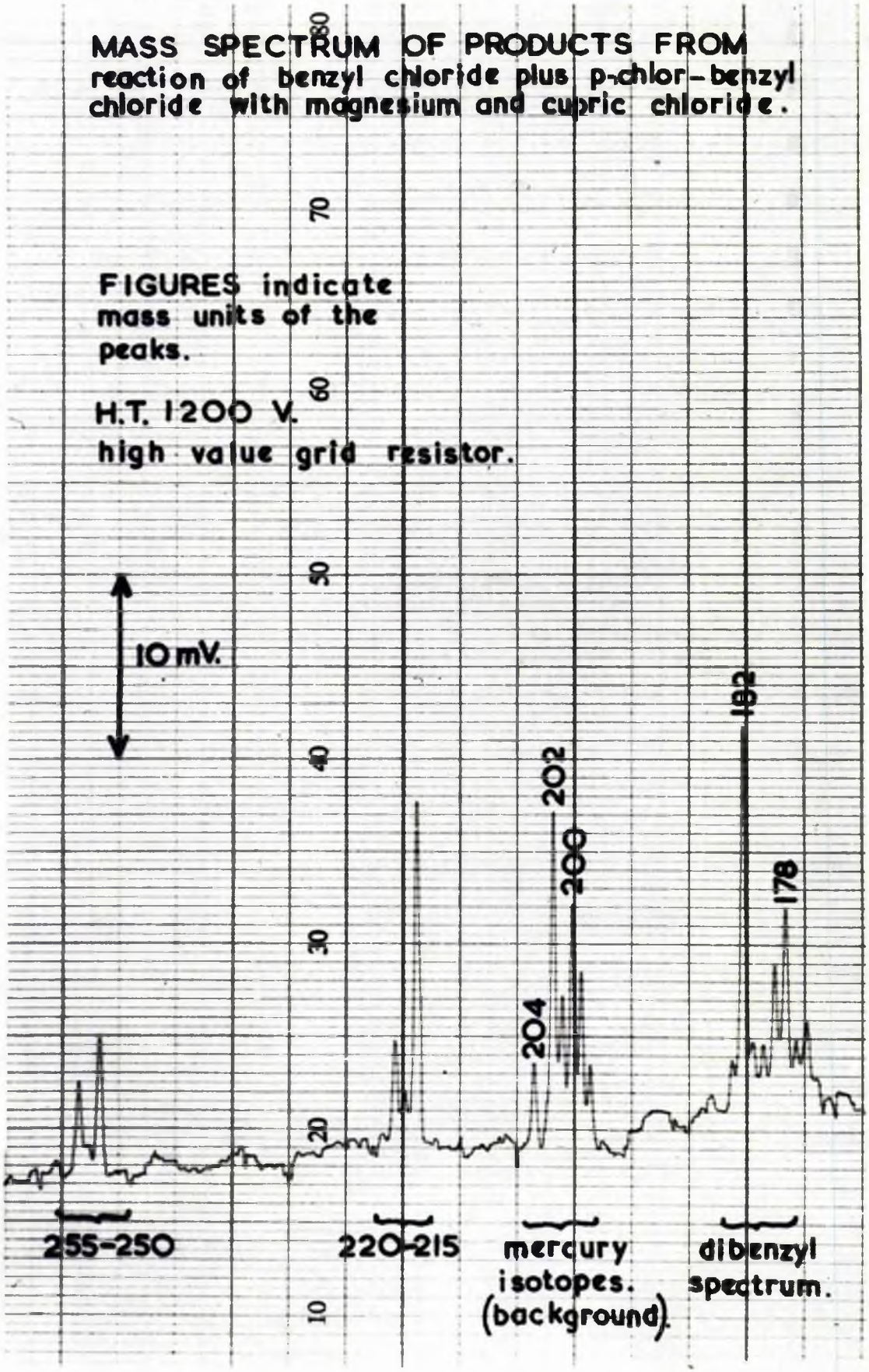
Recrystallisation of the p-chlordibenzyl from either ethyl alcohol or from petroleum ether (b.pt. 40-60°C.) did not yield materials with appreciably sharper melting points.

A petroleum ether solution of the p-chlordibenzyl was allowed to evaporate slowly and the mother liquors were removed as soon as a few crystals had been deposited. These crystals were sublimed in a vacuum four times, and a material of m.pt. 44.8-45.3°C. (corrected) was obtained.

The ultra-violet absorption spectrum of this material of m.pt. 44.8-45.3°C. is shown in Graph 21. This spectrum resembles closely that for p,p'-dichlordibenzyl (m.pt. 100°C.), Graph 17, except in the wavelength region 263-267 mμ and in the relative intensities of the three main absorption maxima. The similarity of the spectra of these two materials indicates that detection of the cross product in mixtures of the three dibenzyls, using optical spectroscopy, would have been difficult.

FIGURE 28.

Fig. 28.


MASS SPECTRUM OF PRODUCTS FROM
reaction of benzyl chloride plus p-chlor-benzyl chloride with magnesium and cupric chloride.
FIGURES indicate mass units of the peaks.
H.T. 1200 V.
high value grid resistor.
10 mV.
80
70
60
50
40
30
20
10
204
202
200
192
178
255-250
220-215
mercury isotopes. (background)
dibenzyl spectrum.

The synthesis of a mixture of dibenzyl, p-chlordibenzyl and p,p'-dichlordibenzyl.

It was possible to synthesise a mixture of these three materials directly from a mixture of benzyl chloride (1.2 ml.) and p-chlorbenzyl chloride (1.62 gm.) treated with magnesium (0.48 gm.) and anhydrous cupric chloride (2.7 gm.) in a manner similar to that described above on page 110 for the preparation of p,p'-dichlordibenzyl. (73).

The liquid product, which was obtained in 91% yield, slowly deposited crystals. The liquid was analysed by the mass spectrometer with the result shown in Fig. 28. This mass spectrum is seen to be very similar to the mass spectrum shown in Fig. 24, which was obtained from the products of the mixed thermal decompositions of mercury dibenzyl and mercury di-(p-chlorbenzyl) dissolved in iso-octane.

In order to obtain a sample of p-chlordibenzyl, some attempts were made to separate the three components of this liquid product by chromatographic methods on alumina and silica gel columns, using the fluorescent indicator techniques described by Brockmann and Volpers (72). Unfortunately, these attempts were not successful because these compounds did not quench the fluorescence of either morin or zinc silicate.

Discussion.

The decompositions of mercury dibenzyl and mercury di-(p-chlorbenzyl) in dilute solutions in iso-octane followed first-order laws accurately to at least 86% reaction.

It is probable that these decompositions involve the breaking of mercury-carbon bonds and the formation of organic free radicals; this is strongly indicated by the detection of p-chlordibenzyl in the products of the decompositions of mixtures of mercury dibenzyl and mercury di-(p-chlorbenzyl) in iso-octane solution.

This information by itself, however, is not sufficient to determine the reaction mechanism, because there are two mercury-carbon bonds per molecule, and they may break one after the other or simultaneously i.e. the first step in the decomposition might be either

$$Bz\text{-}Hg\text{-}Bz \longrightarrow Bz\text{-}Hg\text{-} + \text{-}Bz \quad - D_1 \text{ kcal.} \qquad (I)$$

followed by $$Bz\text{-}Hg\text{-} \longrightarrow Bz\text{-} + Hg \quad - D_2 \text{ kcal.},$$

or $$Bz\text{-}Hg\text{-}Bz \longrightarrow Bz\text{-} + Hg + \text{-}Bz - (D_1 + D_2)\text{kcal.} \quad (II).$$

The products obtained from this decomposition indicate that further reaction is exclusive dimerisation of the benzyl radicals

$$Bz\text{-} + \text{-}Bz \longrightarrow Bz\text{-}Bz ,$$

presumably requiring zero or very small activation energy. The most likely alternative, the attack of benzyl radicals on the solvent molecules

$$Bz\text{-} + H\text{-}S \longrightarrow Bz\text{-}H + \text{-}S ,$$

would be at least 15 kcal. endothermic, and is unlikely at the

low temperatures of these experiments. Porter and Windsor (86) have shown that benzyl radicals can exist in solution, and they have followed the dimerisation process.

An examination of the energies of activation obtained for the decompositions, together with other thermochemical data, could assist in making a decision between these alternative decomposition schemes.

The simple view that the rate determining step in the decomposition is reaction (I) would relate the bond dissociation energy of the first broken mercury-carbon bond, D_1(BzHg-Bz), to the energy of activation for this reaction, on the usual assumption of zero activation energy for the reverse recombination step.

If the decomposition occurred by route (II), however, we would expect the energy of activation to approximate to $(D_1 + D_2)$.

Unfortunately, there is at present insufficient thermochemical data available for mercury dibenzyl to obtain the appropriate values of D_1 and $(D_1 + D_2)$. In general, however, it would be expected that D_1(BzHg-Bz) would be less than D_1(MeHg-Me) in mercury dimethyl, and that the difference between these quantities could be ascribed to the resonance energy of the benzyl group.

D_1(MeHg-Me) is now well established as (51.3 ± 0.5) kcal./mole from work with mercury dimethyl in the gas phase (94), (95), but the resonance energy of the benzyl group is a quantity whose value is known with less certainty.

$D(CH_3-H)$ is well established to be 101-102 kcal./mole (18). The pyrolysis of toluene produced $D(PhCH_2-H)$ as 77.5 kcal./mole (87), while studies of the bromination of toluene gave 89.5 kcal./mole for the same quantity.(88). Benson and Buss have determined $[D(PhCH_2-H) - D(PhCH_2-Br)]$ from the equilibrium position in bromination, and prefer a value of 84-85 kcal./mole for $D(PhCH_2-H)$, although they did not actually determine this quantity separately (89). From the above data we deduce resonance energies of between 11.5-24.5 kcal/mole for the benzyl radical.

Recent work by Alexander (90) and Davidson (59) has attempted to discriminate between these values by determining $D(PhCH_2-CH_2Ph)$, for which they quote values of 61 kcal./mole and 60 kcal./mole respectively. This compound has a central carbon-carbon bond which is weakened by the resonance energies of two benzyl groups, and therefore their determinations provide a sensitive test between the various values for the resonance energy. The value of 60-61 kcal./mole for $D(PhCH_2-CH_2Ph)$ is in agreement with 85 kcal./mole for $D(PhCH_2-H)$.

Taking (16.5 ± 2) kcal./mole as a reasonable value for the resonance energy of the benzyl group, we can estimate the bond dissociation energy of the first mercury-carbon bond in mercury dibenzyl, thus :-

$$D_1(MeHg-Me) - D_1(BzHg-Bz) = (16.5 \pm 2)$$

$$(51.3 \pm 0.5) - D_1(BzHg-Bz) = (16.5 \pm 2)$$

$$\text{or} \qquad D_1(BzHg-Bz) = (34.8 \pm 2.5) \text{ kcal./mole.}$$

This data refers, of course, to the gaseous phase decomposition of mercury dibenzyl.

The experimentally observed energy of activation for the decomposition of mercury dibenzyl in solution is (38.8 ± 0.36) kcal./mole which lies just outside the upper limit of the value estimated above for D_1(BzHg-Bz) in the gas phase decomposition of the material.

The high values of the temperature-independent factors obtained for these decompositions, however, makes it necessary to inquire into the significance of the E_A values, and to question their relation to the energy required for any specific process in the molecules.

In reactions in solution, the molecules of the reactant, the transition complex and the products are solvated, possibly to different extents, so that the energy for a dissociation process may not refer directly to a property of the unsolvated reactant molecule.

There are, however, several reactions which involve neither chain processes nor ions, which proceed with higher temperature-independent factors than expected, in both the gas phase and in solution, and in these instances the effect of the solvent may be concluded to be slight (or self-cancelling). Some illustrative data are given below for the decomposition of di-t-butyl peroxide. In this example, the primary reaction is assumed to be the fission of the RO-OR bond to yield two free radicals; the observed energy of activation lies close to the

value calculated for the strength of the RO-OR bond in the molecule. The reaction is discussed in (91).

Solvent	$(A\ sec^{-1}) \times 10^{-16}$	E_A kcal./mole
Gas phase	3.2	39.1
iso-propyl benzene	0.6	37.5
t-butyl benzene	1.1	38
tri-n-butyl amine	0.35	37
Calculated RO-OR bond strength		38

In current views on unimolecular dissociations it is often considered that a normal temperature-independent factor is about $10^{13} - 10^{14}$, this being the order of bond vibration frequencies. Pritchard (92) has considered the decomposition of the mercury organic compounds given in Table 12, where a considerable rise in the temperature-independent factor occurs as the organic groups attached to the central mercury atom become more complex. He discusses the two modes of decomposition analogous to (I) and (II) above, and by using the formula for a unimolecular decomposition :-

$$k = \lambda \cdot \exp(-\epsilon/RT) \sum_{r=0}^{s-1} \frac{1}{\underline{r}} \left(\frac{\epsilon}{RT}\right)^r ,$$

where s is the number of internal vibrations contributing to the reaction co-ordinate, he has shown that an increasing value of s is required to account for the observed pre-exponential factors in the Arrhenius equation. By considering the HgR_2 molecules as similar to linear tri-atomic systems he suggested that only the antisymmetric vibration could cause decomposition by mode (I) (i.e. the value of s is 1), while for mode (II) the

TABLE 12

and

TABLE 13.

Table 12.

The results of the pyrolyses of several organo-mercury compounds.

Compound	$A_{obs.}$ $sec.^{-1}$	E_a kcal. per mole	Mode of decomp. ϕ	$D_1 + D_2$ ‡
$HgMe_2$	3.0×10^{13}	51.3	I (+II?)	59 ± 4
$HgEt_2$	1.3×10^{14}	42.5	I + II	50 ± 6
$Hg(n\text{-}Pr)_2$	3.3×10^{15}	47.1	II + I	48 ± 9
$Hg(i\text{-}Pr)_2$	4.3×10^{15}	39.3	II + I	41 ± 7
$HgPh_2$	$1. \times 10^{16}$	68.0	II	63 ± 8
$HgBz_2$	1.8×10^{16}	38.8	II	-
$Hg(p\text{-}ClBz)_2$	1.0×10^{16}	38.1	II	-

ϕ Modes of decomposition I $R\text{-}Hg\text{-}R \longrightarrow R\text{-}Hg\text{-} + \text{-}R$
II $R\text{-}Hg\text{-}R \longrightarrow R\text{-} + Hg + \text{-}R$

The first-indicated mode predominates.

‡ Data presented by Warhurst (93).

Table 13.

Observed and calculated rate constants ($sec.^{-1}$) for mercury dibenzyl.

Parameters ϕ	373°A.	403°A.	433°A.
Observed values	3.2×10^{-7}	1.6×10^{-5}	4.6×10^{-4}
$\epsilon_I = 34.8$, s = 1	5.7×10^{-8}	1.9×10^{-6}	3.8×10^{-5}
$\epsilon_{II} = 40.8$, s = 3	2.7×10^{-8}	1.4×10^{-6}	4.2×10^{-5}
$\epsilon_{II} = 40.8$, s = 4	5.1×10^{-7}	2.4×10^{-5}	6.8×10^{-4}

ϕ The ϵ values are in kcal.

The rate equation obtained from the calculated values of the rate constants in the last line of Table 13 is :

$$\log_{10}(k_{1\ calc.}\ sec.^{-1}) = 16.29 - (38{,}500/4.57\ T).$$

The experimentally observed rate equation for the decomposition is:

$$\log_{10}(k_{1\ obs.}\ sec^{-1}) = 16.25 - (38{,}800/4.57\ T).$$

contributing vibrations could cause s to have a maximum value of 4. In his calculations, Pritchard took $\epsilon_I = D_1$ for mode (I) decompositions and $\epsilon_{II} = D_1 + D_2$ for mode (II) decompositions and within the limits mentioned he succeeded in accounting for the enhanced pre-exponential factors indicated in Table 12 by supposing a shift in decomposition behaviour from mode (I) for $HgMe_2$ to mode (II) for $HgPh_2$, with mixed type of behaviour for the other cases.

It is possible to perform calculations for mercury dibenzyl similar to those of Pritchard's for the other mercury compounds if our estimate of D_1(BzHg-Bz) = 34.8 kcal./mole is used in conjunction with an assumed value of D_2 = 6 kcal./mole. (It is likely that D_2 will be small; Pritchard assumed this value for D_2 for all his calculations. The value of D_2 has been given more recently as ca. 8 kcal./mole (93) based on D(Hg-H)).

Thus, $\lambda = 1.5 \times 10^{13}$ sec.$^{-1}$ (Pritchard) and $\epsilon_I = 34.8$ kcal./mole and $\epsilon_{II} = 40.8$ kcal./mole inserted in the formula quoted above give the results quoted in Table 13 for the various s values.

It is a well known consequence of the above formula for a unimolecular dissociation that the experimental activation energy E_A is represented by $\left[\epsilon - (s-1)RT\right]$. Thus at 400°K the energy of activation E_A observed would be subject to a correction when s = 4 of about 2.4 kcal./mole in order to get the effective ϵ value for the equation and for the process involved. The effective ϵ value would thus be (38.8 + 2.4) kcal./mole, which is in good agreement with the ϵ_{II} value deduced above, considering

the uncertainties involved.

In the absence of firm data on D_1 and D_2 we cannot reach definite conclusions on the interpretation of the experimental pre-exponential or energy of activation values, but it seems most probable that the decompositions of mercury dibenzyl and the related mercury di-(p-chlorbenzyl), in iso-octane as solvent and in the absence of air, occur mainly by the initial simultaneous split of both mercury-carbon bonds in the molecules concerned, thus yielding benzyl or p-chlorbenzyl radicals and mercury.

Summary.

1. The author collaborated with Mr. A.M. Hamer and Mr. R.C. Naylor during the construction of a mass spectrometer. A description of this instrument is given.

2. A scheme for the mass spectrometric study of the gas phase decomposition of mercury dibenzyl was abandoned because the substance decomposed in the solid state at 100°C., when the vapour pressure was only 10^{-3}mm.

3. Mercury dibenzyl was prepared which was 99.5-99.8% pure by analysis, and its decomposition was studied in iso-octane solution, after preliminary work in decalin and n-hexane.

4. In the absence of air the decomposition in iso-octane was first-order (up to at least 90% decomposition), and followed a first-order law with

$$\log_{10}(k_1 \text{ sec.}^{-1}) = (16.25 \pm 0.19) - (38,800 \pm 360)/4.57\ T,$$

over the temperature range 100-156°C. (The errors quoted are standard errors).

The reaction rate was followed by absorption spectrophotometry. The products were identified as mercury and dibenzyl.

5. Mercury di-(p-chlorbenzyl) was prepared and analysed 98.9% pure. In the absence of air it decomposed in iso-octane solution by a first-order law with velocity constants given by

$$\log_{10}(k_1 \text{ sec.}^{-1}) = (16.00 \pm 0.15) - (38,100 \pm 290)/4.57\ T,$$

over the temperature range 100-160°C., and up to at least 86% decomposition. (The errors quoted are standard errors).

The products were shown to be mercury and p,p'-dichlordibenzyl.

6. Mixtures of mercury dibenzyl and mercury di-(p-chlorbenzyl) when decomposed in iso-octane gave mercury, dibenzyl, p,p'-dichlordibenzyl and p-chlordibenzyl.

The organic products were identified by mass spectrometric analyses.

6 (Continued).

The relative quantities of these products suggests that radicals are produced during the decompositions, and that they have considerable freedom of movement away from the site of formation.

7. A discussion of the results is given in relation to other thermal decomposition data for mercury di-alkyl and di-aryl compounds. At present this is handicapped by lack of information on the endothermicities of:-

$$BzHgBz \longrightarrow -HgBz + Bz-$$

and $$-HgBz \longrightarrow Hg + Bz- \quad .$$

APPENDIX 1.

The data for Experiment 17/I.

Original Solution No. 5 was used. (See Appendix 4).
Ten vessels, each containing 1 ml. of the original solution, were sealed after the liquid had been degassed.
The thermostat temperature was 129.5°C. (corrected).
For all the analyses below, 0.05 ml. of the solutions were taken with a self-setting micro-pipette (used as a content pipette) and were diluted with solvent to 1.1 ml., using a specially constructed standard flask.
The figures recorded are the average of five optical density readings, obtained with the solutions in a silica cell of 0.2 cm. optical path, against the solvent in a similar cell as standard.

Slit mm.	λ mμ.	O.S.	No.1	No.2	No.3	No.4	No.5	No.6
1.4	210	0.923	0.885	-	0.880	0.832	0.847	0.807
0.6	215	0.575	0.562	-	0.560	0.539	0.547	0.520
0.44	220	0.368	0.361	-	0.360	0.347	0.351	0.338
0.5	225	0.325	0.318	-	0.299	0.275	0.280	0.259
0.3	230	0.334	0.328	-	0.306	0.281	0.284	0.260
0.3	242	0.432	0.429	-	0.397	0.362	0.367	0.339
0.3	250	0.558	0.558	-	0.510	0.466	0.472	0.430
0.3	255	0.583	0.578	-	0.530	0.481	0.487	0.442
0.3	259	0.566	0.561	-	0.513	0.471	0.474	0.433
0.3	272	0.377	0.370	0.342	0.341	0.312	0.316	0.288
0.3	280	0.250	0.243	0.220	0.226	0.208	0.210	0.190
0.3	285	0.181	0.176	0.165	0.166	0.151	0.154	0.139
0.3	290	0.127	0.122	0.116	0.117	0.105	0.106	0.097

Slit mm.	λ mμ.	No.7	No.8	No.9	No.10
1.4	210	0.760	0.706	0.730	0.438
0.6	215	0.496	0.474	0.492	0.341
0.44	220	0.321	0.306	0.319	0.214
0.5	225	0.229	0.196	0.208	0.029
0.3	230	0.229	0.193	0.200	0.009
0.3	242	0.296	0.252	0.262	0.018
0.3	250	0.379	0.319	0.328	0.015
0.3	255	0.391	0.329	0.333	0.012
0.3	259	0.380	0.320	0.322	0.012
0.3	272	0.252	0.210	0.212	0.002
0.3	280	0.165	0.138	0.138	0.001
0.3	285	0.122	0.101	0.102	0.001
0.3	290	0.085	0.071	0.072	0.001

Vessel No.	Duration of heating.
1	Sealed but unheated.
2	1 hr. 31 mts.
3	1 hr. 31 mts.
4	3 hrs. 1 mt.
5	3 hrs. 1 mt.
6	4 hrs. 30 mts.
7	6 hrs. 46 mts.
8	9 hrs. 32 mts.
9	9 hrs. 32 mts.
10	167 hrs. 4 mts., for products.

APPENDIX 2.

The data for Experiment 34/I.

Original Solution No. 2 was used. (See Appendix 4 (b)).

Ten vessels, each containing 1 ml. of the original solution, were sealed after the liquid had been degassed four times.

The thermostat temperature was 159.5°C. (corrected).

For all the analyses below, the solutions were placed directly in a silica cell of 0.2 cm. optical path, and five optical density readings were obtained at each wavelength (ten readings were obtained at each wavelength for the products in vessel No. 10), against the solvent in a similar cell as standard.

Slit mm.	λ mμ.	No. 1	No. 2	No. 3	No. 4	No. 5
0.6	223	0.516	0.626	0.618	0.684	0.777
0.3	272	0.925	0.693	0.694	0.496	0.398
0.3	277	0.758	0.578	0.578	0.419	0.336
0.3	285	0.506	0.388	0.384	0.272	0.218

Slit mm.	λ mμ.	No. 6	No. 7	No. 8	No. 9	No.10
0.6	223	0.716	0.793	0.840	0.816	0.892
0.3	272	0.370	0.288	0.232	0.225	0.043
0.3	277	0.313	0.249	0.203	0.197	0.052
0.3	285	0.204	0.156	0.124	0.122	0.020

Vessel No.	1	2	3	4	5	6	7	8	9	10
Duration of heating, minutes.	Sealed but unheated.	9	9	19	27	27	37	45	45	2176

APPENDIX 3.

The examination of the material suspected to be p,p'-dichlordibenzyl by nuclear magnetic resonance spectroscopy.

Introduction.

The author is indebted to Dr. A.N. Hamer for his kindness in examining the compounds mentioned below by N.M.R. spectroscopy, and for his interpretations of the spectra obtained.

The initial oxidation studies on the compound of m.pt. 99.25-100.0°C., obtained from the interaction of p-chlorbenzyl chloride, magnesium and cupric chloride, (which had the same m.pt. and ultra-violet spectrum as the compound obtained from the thermal decomposition of the mercury di-(p-chlorbenzyl)), gave only small yields of materials having acidic properties (see page 111), and an attempt was made to ascertain the structure of the compound with certainty by the use of N.M.R. techniques.

The principles of N.M.R. spectroscopy and the applicability, power and scope of high resolution techniques for the investigation of molecular structures have been reviewed elsewhere (79) to (85).

The investigation.

1. By making the assumptions :-

   (a) that the molecular formula of the compound was $C_{14}H_{12}Cl_2$, and

   (b) that it was a pure compound,

it was possible to prove that the spectrum observed with this material was consistent with a compound having a dibenzyl-type carbon skeleton with two chlorine atoms, one in each para-position. Assumption (a) was justified from the mass spectrum of the material (Figure 26), whilst the small m.pt. range of the material suggested a compound of reasonable purity.

2. A preliminary examination of the compound by N.M.R. showed two bands corresponding to those expected for aromatically and aliphatically bound protons. The ratio of the area under the aromatic band to that under the aliphatic band was 2.0 ± 0.05, thus suggesting 8 aromatic and 4 aliphatic protons per molecule.

   Structures consistent with this evidence included :-

   (a) a diphenyl-type skeleton with ($-CH_2Cl$, $-CH_2Cl$) or

($-CH_2CH_2Cl$, $-Cl$) or ($-CHClCH_3$, $-Cl$) or ($-CCl_2CH_3$, $-H$) or ($-CHClCH_2Cl$, $-H$) or ($-CH_2CHCl_2$, $-H$) or ($-CH_3$, $-CHCl_2$) as substituents.

(b) a diphenyl methane-type carbon skeleton with either ($-CH_2Cl$, $-Cl$) in phenyl substitution or ($-CH_3$, $-Cl$) in the phenyl rings which are joined by a $-CHCl-$ bridge.

(c) a 1,1-diphenyl ethane or a 1,2-diphenyl ethane-type carbon skeleton with two $-Cl$ in the rings.

3. An examination of the aliphatic proton resonance band under conditions of high resolution indicated no trace of complexity, which implied that all four aliphatic protons were equivalent. Two carbon skeletons fulfilled this condition - the diphenyl type with ($-CH_2Cl$, $-CH_2Cl$) substituents, and the 1,2-diphenyl ethane type.

The position of the aliphatic proton resonance band showed that these protons were not bonded to the carbon atoms which carried the chlorine atoms; thus, the diphenyl-type structure had to be eliminated.

4. The position of the two chlorine atom substituents in the 1,2-diphenyl ethane skeleton was decided by a comparison of the N.M.R. spectra from the unknown material with those from authentic samples of the three mono-chlortoluenes. The spectra of the unknown resembled that for the p-chlortoluene, and they differed markedly from the o- and m-chlortoluene spectra. From such comparisons, it was clear that both halogen atoms were substituted in the para- positions of the 1,2-diphenyl ethane.

Hence, the compound of m.pt. 99.25-100.0°C. was concluded to be p,p'-dichlordibenzyl. This was subsequently confirmed by oxidation of this material, as described on page 111.

APPENDIX 4.

(a) Solutions of mercury dibenzyl used for the investigations.

Solution No.	Weight of mercury dibenzyl. mgm.	Volume of iso-octane ml.	Used for Experiments No.
1	17.08	25.0	1/I, 2/I.
2	24.10	25.0	3/I, 4/I, (5/I).
3	18.04	25.0	6/I, 7/I, 8/I.
4	19.49	25.0	9/I, 10/I, 13/I, 14/I.
5	49.65	49.9	15/I, 16/I, 17/I, 18/I, 19/I, 20/I, 21/I.
6	3.38	49.9	22/I, 23/I.
7	26.03	49.9	24/I, 25/I, 27/I, 29/I.
8 ø	1.61	25.0	26/I.
9 ø	1.61	25.0	28/I, 30/I.
10	15.14	49.9	32/I.

ø These solutions were obtained by diluting Solution No. 7.

(b) Solutions of mercury di-(p-chlorbenzyl) used.

Solution No.	Weight of mercury compound. mgm.	Volume of iso-octane ml.	Used for Experiments No.
1.	6.1 ø	49.9	31/I, 33/I.
2.	4.67	49.9	34/I, 35/I, 36/I, 37/I.
3.	4.20	49.9	38/I, 39/I.
4.	6.95	49.9	40/I, 41/I.

ø Calculated from optical densities of the solution.

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